

MODERN ASPECTS
OF
INORGANIC CHEMISTRY

Uniform with this volume

Physical Aspects of Organic Chemistry

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PREFACE TO SECOND EDITION

In preparing a revised edition of this book the authors have attempted to bring the subject matter up to date, without radical changes in the method of presentation.

During the fourteen years which have elapsed since the first edition was published, there has been increased activity in the field of inorganic chemistry (notably on the Continent and in the United States), and a great deal of important new work has appeared. This has made the task of selection difficult, especially as it seemed desirable to avoid any undue increase in the size and cost of the book. In the course of revision, a few topics dealt with previously have, of necessity, been omitted. Thus, a survey of the chemistry of the new elements replaces the account of hafnium, rhenium and the platinum metals. Much of the text has been completely rewritten, and new chapters have been inserted on valency, on the constitution of solid inorganic compounds, and on interstitial and non-stoichiometric compounds.

Some of the topics discussed are in course of rapid development, and what has been written may very soon appear incomplete. On other topics, where the authors have tried to interpret coherently the results of independent schools of work, they may inadvertently have gone beyond the conclusions drawn by the original workers. For such shortcomings, and for any mistakes which may occur, they ask the reader's indulgence. They ask, indeed, that this book be read critically, and that where possible original papers be consulted. The reader cannot then fail to be impressed by the incompleteness of our knowledge of even the most familiar chemical elements.

H. J. E.
J. S. A.

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CHAPTER I

ATOMIC STRUCTURE AND THE PERIODIC SYSTEM

Introduction.—Two distinct approaches to the classification of the chemical elements have been developed during the last hundred years. The first has been evolved primarily from the observed variations in chemical and physical properties in passing from one element to the next. The second, and newer, is based on differences in the atomic structure. A stage has now been reached in the evolution of Chemistry at which these two subjects, which may be called the chemical and physical classification of the elements, can be correlated. We may seek to explain the chemical periodicity in terms of atomic structure, and to place the concepts of valency on a surer physical basis. Such is the object of this first chapter. If it appears that undue emphasis has been placed on the physical aspects of the subject, it must be borne in mind that, although at present less familiar to the chemist than is the descriptive chemistry of the Periodic System, they are assuming a great and increasing importance in current chemical thought.

That there is any systematic connexion between the atomic weights of the elements and their chemical properties was first recognized by Döbereiner in 1829. He directed attention to the existence of triads of related elements, such as calcium, strontium and barium, or chlorine, bromine and iodine, in which the elements occupying the middle position had not only chemical properties intermediate between the other two, but also an atomic weight close to the arithmetic mean of the atomic weights of the others. The next important step was taken in 1863–4, when Newlands pointed out that if the elements known at that time were arranged in order of increasing atomic weight, omitting hydrogen, the first seven (lithium, beryllium, boron, carbon, nitrogen, oxygen and fluorine) were all distinct in their properties. The next element after fluorine, however, was sodium, which had a strong resemblance to lithium, and each of the six elements following (magnesium, aluminium, silicon, phosphorus, sulphur and chlorine) bore an obvious similarity to the corresponding member of the first group of seven. This so-called Law of Octaves could not convincingly be extended to elements of atomic weight higher than that of chlorine.

Table 1

Periodic System of the Elements

0	I		II		III		IV		V		VI		VII		VIII	
	a	b	a	b	a	b	a	b	a	b	a	b	a	b		
2 He 4.003	3 Li 6.940		4 Be 9.013		5 B 10.82		6 C 12.010		7 N 14.008		8 O 16.0000		9 F 19.000			
10 Ne 20.183	11 Na 22.997		12 Mg 24.32		13 Al 26.97		14 Si 28.06		15 P 30.98		16 S 32.066		17 Cl 35.457			
18 Ar 39.944	19 K 39.096		20 Ca 40.08		21 Sc 45.10		22 Ti 47.90		23 V 50.95		24 Cr 52.01		25 Mn 54.93		26 Fe 55.85	27 Co 58.94
	29 Cu 63.54		30 Zn 65.38		31 Ga 69.72		32 Ge 72.60		33 As 74.91		34 Se 78.96		35 Br 79.916			28 Ni 58.69
36 Kr 83.7	37 Rb 85.48		38 Sr 87.63		39 Y 88.92		40 Zr 91.22		41 Nb 92.91		42 Mo 95.95		43 Tc [99]		44 Ru 101.7	45 Rh 102.91
	47 Ag 107.880		48 Cd 112.41		49 In 114.76		50 Sn 118.70		51 Sb 121.76		52 Te 127.61		53 I 126.92			
54 Xe 131.3	55 Cs 132.91		56 Ba 137.36		57-71 RARE EARTHS*		72 Hf 178.6		73 Ta 180.88		74 W 183.92		75 Re 186.31		76 Os 190.2	77 Ir 193.1
	79 Au 197.2		80 Hg 200.61		81 Tl 204.39		82 Pb 207.21		83 Bi 209.00		84 Po 210.0		85 At [210]			78 Pt 195.23
86 Rn 222	87 Fr [223]		88 Ra 226.05		89 Ac 227		90 Th 232.12		91 Pa 231		92 U 238.07		93-?		TRANSURANIC ELEMENTS†	

* Rare earths 57 La 58 Ce 59 Pr 60 Nd 61 Pm 62 Sm 63 Eu 64 Gd 65 Tb 66 Dy 67 Ho 68 Er 69 Tm 70 Yb 71 Lu
138.92 140.13 140.92 144.27 [147] 150.43 152.0 156.9 159.2 162.46 164.94 167.2 169.4 173.04 174.99

† Transuranic Elements 93 Np 94 Pu 95 Am 96 Cm 97 Bk 98 Cf
[237] [239] [241] [242] [243] [244]

Note :—Figures in square brackets represent the mass numbers of the longest-lived or most accessible isotopes of artificial radio-active elements.

The Periodic System was first developed by Mendeléeff in 1869, and with minor modifications due to the discovery of new elements and the correction of atomic weights, the table then suggested is essentially that used for the chemical classification of the elements at the present time (Table 1, opposite). No detailed discussion of the chemical aspects of the Periodic Classification is necessary here. The anomalies presented by the pairs of elements argon and potassium, cobalt and nickel, tellurium and iodine, which have to be placed in the Table in the reverse order of their atomic weights, are accounted for by the relative abundance of their respective isotopes, as is shown in the following table (*see also* p. 20). Thorium and protactinium also have atomic weights which are in the reverse order to their atomic numbers.

Table 2

<i>Element</i>	<i>Atomic number</i>	<i>Atomic weight</i>	<i>Isotopes (in order of abundance)</i>
Argon . .	18	39.944	40, 36, 38
Potassium . .	19	39.096	39, 41, 40
Cobalt . .	27	58.94	59, 57
Nickel . .	28	58.69	58, 60, 62, 61, 64
Tellurium . .	52	127.61	130, 128, 126, 125, 124, 122, 123
Iodine . .	53	126.92	127

The chemical atomic weight measures the average mass of all the atoms of an element, and it is because of the preponderance of the heavy isotope of argon, of mass 40, that its mean atomic weight is greater than that of potassium. Similar considerations apply to the other anomalous pairs.

The position of hydrogen in the Table, formerly much debated, is, in fact, a matter of small importance, since hydrogen and helium stand alone from the point of view of atomic structure. Mendeléeff designated as 'transition elements' the three triads Fe, Co, Ni; Ru, Rh, Pd, and Os, Ir, Pt, assigned by him to Group VIII. The term is now generally used in a wider sense, to include those elements in the centre of the 'long periods', from scandium to zinc, yttrium to cadmium, lanthanum to mercury, and actinium to berkelium (or ultimately, to element 103). In these four series of elements a special type of relationship exists between the structure of each atom and its neighbours, due to the preferential filling of inner rather than the outermost electronic orbits.

Atomic Structure.—Our modern theory of atomic structure is

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based on Rutherford's concept of the atom, as built up from a small, massive, positively charged nucleus, surrounded by a sufficient number of electrons to render the whole structure electrically neutral. Such an atom model was the inescapable conclusion drawn from experiments on the scattering of electrons and of α -particles by matter, which showed that most of an atom must be empty space; strong deflexion of the charged particles is a rare event, occurring when an α -particle passes relatively close to the charged nucleus. Whereas the diameter of the whole atom is of the order 10^{-8} cm., that of the nucleus is only 10^{-12} cm. In this nucleus—itsself, as we now believe, a complex structure—is concentrated almost the entire mass of the atom, whilst the effective 'size' of the atom represents the sphere of action of the extra-nuclear electrons.

A fundamental contribution to the study of atomic nuclei was made in the years 1913–14 by Moseley,¹ who, in the course of an investigation of the relatively simple X-ray spectra of certain of the metallic elements, found that there was an almost linear relationship between the characteristic X-ray frequency for each of a series of elements and the squares of the atomic numbers of the elements (*i.e.* the number assigned to each element when these were arranged in order of increasing atomic weight and numbered consecutively from hydrogen (= 1) to uranium (= 92)). Subsequent developments have proved the atomic number to be more significant from both the physical and the chemical standpoints than the atomic weight. The atomic numbers of the elements are inserted in the Periodic Table which is reproduced on page 2. The nature of the X-ray spectrum needs a little more elucidation than has been given, as it does not consist of a single line, but of several groups of lines, which are known as the K, L, M . . . lines. In testing Moseley's law it is necessary to pick out a particular frequency of one of these groups for each element considered—say, the highest frequency in the K . . . each element. Denoting this frequency by ν and . . . number by Z , Moseley's law may be expressed as

$$\nu = a(Z - b)^2$$

where a and b are constants, *i.e.* there is approximately a linear relationship between Z and $\sqrt{\nu}$.

It follows, then, that if $\sqrt{\nu}$ is plotted against Z , then each element (over a certain range) must be represented by a point on the resulting straight line. The *order* of the elements in the Periodic System, as required by the chemical evidence, was unambiguously confirmed

¹ *Phil. Mag.*, 1913, [vi], 26, 1024; 1914, [vi], 27, 703.

by this work of Moseley's, and the *number* of the elements, up to and including the heaviest atomic species then known (uranium), was proved to be finite, since Z must be a whole number. Moseley measured the characteristic frequencies of sufficient elements to confirm the order of the rare earth elements, and to show that uranium must have $Z = 92$; of the elements from hydrogen to uranium he showed that six, with atomic numbers 43, 61, 72, 75, 85 and 87, were missing at that time. Two of these elements have since been discovered as stable atomic species—hafnium (72), discovered by Coster and Hevesy in 1924, and rhenium (75), discovered by Noddack and Noddack in 1926. It seems probable that no stable nuclei of the other elements exist in Nature, but radioactive elements of atomic numbers 43, 61, 85 and 87 are now known, either as members of the natural radioactive families, or as products of nuclear reactions (see Chap. XVIII).

The great significance of Moseley's work from the point of view of atomic structure lies in his suggestion that the atomic number of an element is identical numerically with the positive electrical charge on the nucleus. The unit of positive electricity is the charge on the proton, and on this basis the hydrogen nucleus has a charge of $+1$, and this value increases by unity as we come to each succeeding element until at the end of the list of natural elements we have the uranium atom, with a nuclear charge of $+92$. Moseley's suggestion has since been verified by Chadwick's measurements of the deflexion of α -particles in passing through metallic foils, and is fundamental in all modern work on the quantitative aspects of atomic structure.

The magnitude of the nuclear charge fixes at once the number of electrons in the extra-nuclear structure of the atom, since the atom as a whole is neutral. Thus hydrogen will have one such electron, helium two, lithium three, and so on, until in the case of uranium there will be ninety-two electrons surrounding a small massive nucleus with a positive charge of ninety-two units. The arrangement of these extra-nuclear electrons holds the key to the correlation between atomic structure and chemical properties.

The Extra-Nuclear Structure.—The foregoing considerations afford in themselves a rough picture of atomic structure. The mass of the atom must reside in the small central nucleus, and the number of electrons surrounding the nucleus is determined by the positive nuclear charge. The three problems that now present themselves are, firstly, how the electrons are arranged; secondly, how that electronic arrangement can be correlated with the chemical properties of the elements; and thirdly, what happens to the electronic arrangement when chemical combination occurs. It has been

one of the achievements of theoretical physicists to elaborate the nuclear atom model into a rigorous and quantitative theory, answering these problems.

We may note, at the outset, that two views are current as to the nature of an electron. The first, adequate to explain a large range of experimental facts, is that the electron in an atom is a minute particle of mass $1/1840$ part of the mass of a proton, and charge equal to $-e$, moving in a definite orbit around the nucleus. The second, and more recent view, required to interpret certain phenomena, is that the electronic charge is not localized in a small element of space, but that there is a probability function which represents its distribution at any time. For very many purposes of physical and chemical theory, the idea of electrons moving in orbits of different energies is a satisfactory approximation. It had its origin in the postulates made by Bohr in explaining the spectrum of the hydrogen atom, and was elaborated by Bohr, Sommerfeld and others into a comprehensive general theory.

According to classical electromagnetic theory, a circulating electron would continuously radiate energy. To overcome this difficulty, Bohr postulated that atomic phenomena must be subject, not to classical dynamics, but to quantum laws. In particular, the total energy of an electron can assume only certain values, proper to a range of permitted orbits, which he termed *stationary states*, in which it circulates without radiating energy. When an electron passes from one stationary state to another, radiation is either emitted or absorbed, the difference in energy of the two states being related to the frequency of the radiation emitted or absorbed, by the relation

$$E_1 - E_2 = h\nu$$

The greater the energy difference between the stationary states 1 and 2, the higher is the frequency of the radiation absorbed or emitted—*i.e.* the shorter its wave-length. There is evidence that the electrons are arranged around the nucleus in a series of 'shells', each with a limited number of orbits. Transitions between energy states of the outermost shell of the atom give rise to absorption or emission of the optical spectrum, whilst when electrons are displaced from the inner and deep-seated shells, the X-ray spectrum is excited.

The X-ray and visible or ultra-violet spectra of the elements have been widely studied, and for many elements they have been analysed in great detail. The result of this analysis has been that all of the lines observed in the spectrum of any element can be accounted for by transitions between a limited number of definite

electronic states of the atom. Properly interpreted, indeed, the optical and X-ray spectra of an atom give a complete picture of the possible electronic orbits within the atom, their energy, and the distribution of electrons amongst them. The state of the atom in which all the electrons are in the orbits of lowest energy is referred to as the *ground state*, and can also be deduced from the spectroscopic data.

Bohr showed that his postulates lead at once to the calculation of the energy E_n of an electron in a hydrogen-like atom (*i.e.* an atom with one electron only) and a nuclear charge $+Ze$. E_n is, in fact, given by

$$E_n = -\frac{2\pi^2 Z^2 e^4 m}{h^2} \frac{1}{n^2}$$

In this expression Z is the atomic number, e and m are the electronic charge and mass respectively, h is the Planck constant and n , which is termed the principal quantum number, can have the values 1, 2, 3, etc. The energy is least (*i.e.* the state is most stable) when $n = 1$, and increases (becomes less negative) as the value of n increases. Transitions between orbits, defined in this manner by fundamental natural constants, reproduce quantitatively the spectra of hydrogen, ionized helium (He^+), etc. When $n = 1$, the electrons are referred to as K electrons, and are said to be in the K shell. Electrons in orbits for which $n = 2, 3, 4 \dots$ are similarly referred to as in the L, M, N \dots shells respectively.

In atoms with more than one orbital electron, the energy relations are more complex. Although an integral *principal quantum number* n can be assigned to each electron, this quantum number alone is not sufficient to account for all the lines in the spectra of the elements. It is necessary to specify three other quantum numbers which, in effect, bring about a sub-division of the energies of the electrons in the main quantum shells. Thus, for each value of the principal quantum number n there are n sub-levels, distinguished from one another by a new quantum number l , the *azimuthal or subsidiary quantum number*. As originally conceived, the value of l determined the ellipticity of the orbit, for in a many-electron atom, electrons moving in highly elliptic orbits would move in a variable field of force compounded of the attraction of the nucleus and the repulsion of other electrons. The effect of this would be to make the orbits precess. l defines directly the angular momentum A of the electron in its orbit; this is quantized, and can assume only certain values which are given by

$$A^2 = \frac{h^2}{4\pi^2} l(l+1)$$

l can have the values $0, 1, 2 \dots (n - 1)$ when the principal quantum number is n . Electrons with $l = 0, 1, 2, 3 \dots$ are called $s, p, d, f \dots$ electrons respectively. This nomenclature is a survival of an old and empirical notation (s = sharp, p = principal, d = diffuse, f = fundamental) which was based on the appearance of spectral lines due to electron transitions involving these levels. The usual method of describing an electron is to give the numeral representing the principal quantum number first and then the letter, representing the azimuthal quantum number; thus a $3p$ electron would have $n = 3, l = 1$, while a $1s$ electron would have $n = 1$ and $l = 0$. It should also be noted especially that the possible values of l depend on the value of n , as is shown below.

K shell	$n = 1$	$l = 0$ (s electrons only)
L	$n = 2$	$l = 0, 1$ (s, p electrons)
M	$n = 3$	$l = 0, 1, 2$ (s, p, d electrons)
N	$n = 4$	$l = 0, 1, 2, 3$ (s, p, d, f electrons)

The introduction of a third quantum number, the magnetic quantum number m , is necessary to account for the Zeemann effect—the splitting of spectrum lines into several components when the source emitting them is situated in a strong magnetic field. This effect, which implies that orbits defined by the same n and l are identical in energy ('degenerate') only in the absence of a mag-

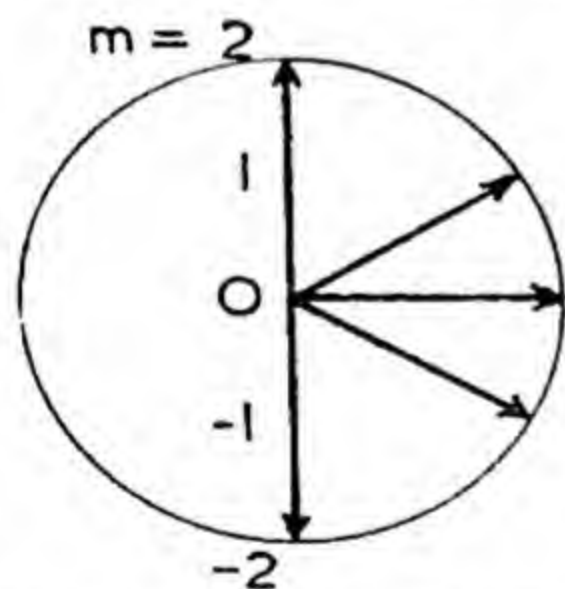


FIG. 1.—Possible orientation of the l vector and corresponding m values for $l = 2$.

netic field, has been interpreted as follows. The orbital angular momentum, measured by l , is a vector quantity. If an external magnetic field is superimposed on the field of the nucleus, the electronic orbits take up a definite orientation with respect to the field, but according to quantum principles, only those orientations are possible for which the component of the orbital angular momentum in the direction of the magnetic field is quantized also. As may be seen from Fig. 1, this component m may have any of the $2l + 1$ values $l, l - 1 \dots 0 \dots -l$. The effect of the magnetic

field is to replace the single stationary state n, l by $2l + 1$ sub-levels, of slightly differing energy, defined by the third quantum number m .

Finally, to account for the multiplet structure of spectrum lines, it is necessary to assign to each electron a fourth quantum number s , the spin quantum number which can have the two values $\pm 1/2$

or $-1/2$. This may be thought of as measuring the angular momentum $\left(\pm \frac{1}{2} \cdot \frac{h}{2\pi}\right)$ of an electron spinning about its own axis.

One other important principle must be introduced in order to see how the four quantum numbers n , l , m and s fix the number of electrons accommodated in each shell of the atom. This is known as the Pauli Exclusion Principle, and it states that no two electrons in the same atom can have the same values for the four quantum numbers n , l , m and s . This means, in effect, that every electron in an atom differs from every other electron in total energy, and that there can be as many electrons in each of the shells as there are possible arrangements of the quantum numbers.

For the first four shells, taking the permissible variations of n , l and m , we then obtain the numbers of possible electron orbits set out in Table 3.

Table 3

Shell	n	l	m	Total	
K . . .	1	0	0	1	1
L . . .	2	0	0	1	
		1	1, 0, -1	3	4
M . . .	3	0	0	1	
		1	1, 0, -1	3	
		2	2, 1, 0, -1, -2	5	9
N . . .	4	0	0	1	
		1	1, 0, -1	3	
		2	2, 1, 0, -1, -2	5	
		3	3, 2, 1, 0, -1, -2, -3	7	16

These totals of 1, 4, 9, 16 do not take into account the spin quantum number; each orbit can accommodate two electrons with $s = +1/2$ and $s = -1/2$ respectively. We accordingly find the maximum number of electrons in the K, L, M and N shells to be 2, 8, 18 and 32 respectively. These numbers, arrived at from a consideration of spectroscopic data, will be recognized as related to the numbers of elements in the various periods of the Periodic Table. Thus the first two short periods contain eight elements each, the first and second long periods contain eighteen elements each, and the third long period contains thirty-two elements. It is, indeed, evident that the periodicity in chemical properties must be derived in some very direct manner from the similar electron arrangements in the outer valency shell of the atoms.

The allocation of all the electrons in each atom to definite orbits

is in a sense a joint triumph for the chemist and the physicist, for it is an undeniable fact that the Periodic Table and a knowledge of the valency of the elements has been of great service in interpreting the physical data. Table 4 (p. 11) shows how the electrons are believed to be arranged. It is seen that the K shell, which can contain only two electrons, is completed in helium, and that all elements with more than two electrons have the K shell full. Similarly between lithium and neon the 2s and 2p orbits are being filled. For $n = 2$, l can have the values 0, 1, while m can have the value 0, and 0 or ± 1 for $l = 0$ and $l = 1$, respectively, and s can be $\pm 1/2$. Thus there are only 8 possible orbits in the L shell, and, after neon, the next element, sodium, has the new electron in a 3s orbit. The process of building up of the 3s and 3p orbits then continues until argon is reached. Argon, like neon, krypton, xenon and radon, has the s and p orbits in its outer shell completely filled. This particular configuration, commonly referred to as a closed shell, is very stable. The resultant orbital angular momentum and electronic spin are both equal to zero, so that the interaction of external systems, *e.g.* electric or magnetic fields, is minimized.

After argon the next two elements, potassium and calcium, accommodate the new electron normally in the two 4s orbits, but in the next element, scandium, it is the 3d orbit instead of the 4p orbit, which takes the added electron. In the following elements from scandium to zinc the ten 3d orbits are occupied in preference to orbits in the incomplete N shell. Two questions immediately present themselves at this point, namely, how is it known that this is so, and why do the electrons go preferentially into the M shell in 3d orbits after having started to fill orbits in the N shell? The evidence for this assignment of electrons is spectroscopic. The spectra of the elements in question show that the orbits to which the electrons have been assigned are the ones of the lowest total energy, and for this reason they are occupied preferentially. It will be noted that in chromium an electron is represented as having left the 4s and reverted to the 3d orbit, while the same thing has happened in copper. This will be referred to later in connexion with variable valency, but it may be stated here that there is often only a small difference in energy between two such alternative orbits, so that an electron can be transferred from one to the other quite easily. These elements in which inner orbits are being filled in preference to outer orbits are called transition elements.

With element 30, zinc, the 3d orbits are full and the M shell has its full complement of 18 electrons. From gallium (31) to krypton (36) the 4p orbits are filled, after which in rubidium and strontium the 5s orbits are occupied. Then, however, from yttrium to cadmium

The Electron Groups of the Periodic Table

For the electronic structure of elements 93-8, see Chap. XIII. These elements (and possibly U also) have electrons in the 5f orbit.

$4d$ orbits are occupied in preference to $5p$ orbits. The reason for this reversion is again that the energy of such orbits is lower. These ten elements constitute the second transition group. The elements succeeding them, as far as barium, have first the $5p$ and then the $6s$ orbits occupied, after which, in lanthanum, an electron goes to a $5d$ orbit. In the following fourteen elements, however, the added electrons go into $4f$ orbits, although the $5d$ and $6p$ orbits are also available. The reason for this behaviour is the same as in the case of the transition elements; the total energy of such an electron is less in the $4f$ than in the alternative orbits. The elements in which the $4f$ orbits are being filled are the rare earths, and we find in the fact that only an inner shell of electrons is changing a ready explanation of why the valency and general chemical character remains substantially the same throughout the group.

After the rare earths there is a third group of transition elements (Hf to Pt inclusive) in which the $5d$ orbits are being occupied, and from thallium to radon the $6p$ orbits are being filled. Radon itself has the characteristic inert gas structure with a complete octet of electrons in the outer shell. The last elements mark the commencement of a fourth group of transition elements in which inner orbits are occupied in preference to the $7p$. By analogy with the preceding series, either $5f$ orbits or $6d$ orbits might come in question here. The chemical analogies of thorium, protactinium and uranium to hafnium, tantalum and tungsten, rather than to actinium, indicates that as far as uranium, at least, the $6d$ orbits are occupied preferentially. There is some theoretical justification for the view that the stability of $5f$ orbits should become comparable with that of $6d$ orbits at about $Z = 92$, and the chemical properties of the newly discovered 'transuranic' elements, as far as they are known, are compatible with the view that $5f$ orbits are increasingly favoured as the atomic number increases beyond 92. As far as is known, curium ($Z = 96$) is uniformly trivalent and rare-earth like in properties, and probably has 7 electrons in the $5f$ shell.

The Wave-Mechanical Atom.—The theory of atomic structure developed in the preceding section is based on the original conception of an electron as a charged particle, moving according to the laws of mechanics in a definite orbit. In 1924 de Broglie suggested that an electron, or indeed any material particle, could be regarded alternatively, and with equal truth, as undulatory in character; a travelling train of waves, with a wave-length determined by the energy of the electron. This idea was verified when Davisson and Germer (1927) and G. P. Thomson (1928) discovered that a beam of electrons underwent diffraction by a crystal lattice, in the same way as a beam of X-rays of similar equivalent wave-length. At

about the same time the mechanics of the electron waves were developed by Schrödinger (1926) and others. For any explicit discussion of the new quantum mechanics, the reader is referred to other sources. The essential features of atomic structure, discussed already, fall quite naturally into place, however, in the newer outlook, and a qualitative understanding of the quantum mechanical atom is of considerable value in discussing the problem of valency.

The quantum mechanical electron is described mathematically in a form (Schrödinger's equation) similar to the equations of harmonic motion in ordinary dynamics. If the potential field in which the electron moves is specified, the energy of the electron can be related to a quantity, usually represented as Ψ , the solution of the Schrödinger differential equation, which is formally equivalent to the amplitude of the electron wave. In general, Ψ is a complex quantity, but the product $\Psi \cdot \bar{\Psi}$ (where $\bar{\Psi}$ is the complex conjugate of Ψ) is real, and may be regarded as measuring the electron density, that is, the probability of finding an electron in any element of volume.

An electron travelling in free space is formally analogous to a wave propagated in the same direction. An electron moving in any periodic field—as for example in a closed orbit—is, however, comparable with the stationary wave pattern of some harmonic oscillator. Such waves have some suggestive properties, as may be seen by considering the one- or two-dimensional mechanical analogy of a stretched string or a vibrating disc. The equation of harmonic motion in such cases has more than one solution, corresponding to the fundamental vibration and its harmonics, but the solutions are not independent, and correspond to different energies of vibration. The frequencies (and therefore the energies) of the harmonics are related to that of the fundamental by changes in a whole-number parameter—the order of the harmonic—which thus plays the role of Bohr's principal quantum number. The order of the harmonics determines the number of nodes: thus in a vibrating string the n^{th} vibration has $n - 1$ nodal points. For each spatial co-ordinate which must be introduced into the wave equation, a corresponding whole-number parameter must be introduced to describe fully the harmonics.

For an electron circulating in an orbit about an atom we have, then, a wave equation satisfied by a number of solutions. These solutions correspond to a series of discrete energy states, each characterized by the value assigned to a whole number parameter n , the principal quantum number. The standing wave pattern to which the circulating electron corresponds is three-dimensional, so that the modes of vibration represented by the solutions of the

wave equation are spherical harmonics. The nodes are nodal *surfaces*—which may be spherical shells or diametral planes—and to define each energy state completely three quantum numbers must necessarily be specified. The three quantum numbers n , l and m thus enter as a necessary part of the wave-mechanical description of the electron circulating about an atom, and it is found that the values which can be assigned to l and m are inherently restricted to those which were specified on mechanistic grounds in the preceding sections.

The case of a single electron, circulating in the electrostatic field of the atomic nucleus, can be so framed that the resulting wave function is separable into two factors: (i) A radial wave function, which is a function of the principal quantum number n and the azimuthal quantum number l only. This has the general form

$$R(r) = U(r) \cdot \exp\left(-\frac{r}{na}\right); \quad \text{(ii) An angular wave function, which}$$

describes the variation of Ψ around the atom, as dependent on polar coordinates θ and ϕ , and which is a function of the subsidiary quantum numbers l and m only. The general form here is $A(\theta, \phi) = f(\theta) \cdot \exp(\pm m \cdot i\phi)$. From these wave functions there may be constructed the corresponding radial and angular distribution functions. The former measures the electron density at every point along any radial direction. The angular distribution function measures the probability of finding the electrons along any azimuth, and so varies from zero in each nodal plane to a maximum in certain directions. It may be represented graphically by means of a polar diagram, in which the length of a line drawn at an angle θ measures the value of the distribution function along that direction. The angular distribution function accordingly describes the symmetry of the distribution of electron density.

The general form of the radial and angular wave functions and distribution functions is shown in Fig. 2. The distribution function of an s electron displays spherical symmetry, with $n - 1$ spherical nodal surfaces, on which the electron density falls to zero. The electron density has a maximum at some radius which corresponds closely to the radius of the Bohr orbit: although the electron is not restricted to a particular orbit, it may be said to spend much of its time at about that distance from the nucleus. The number of nodal planes in the wave function is given by l . Hence the p electron wave function has a single nodal plane, which may have any of three spatial orientations corresponding to the value of the third quantum number m . Combining the angular and the radial distribution functions, a p wave function corresponds to a dumb-bell shaped distribution of electron density, which may have its axis along any

of these orthogonal axes. Strictly speaking, this is not the form of p wave function obtained by direct solution of the wave equation, though equivalent to it. For d and f wave functions, with two or three nodal planes respectively, the corresponding electron density distributions are more complex, but in each case the number of independent wave functions is limited to $2l + 1$, as it was on the particulate, or Bohr-Sommerfeld, model of the atom.

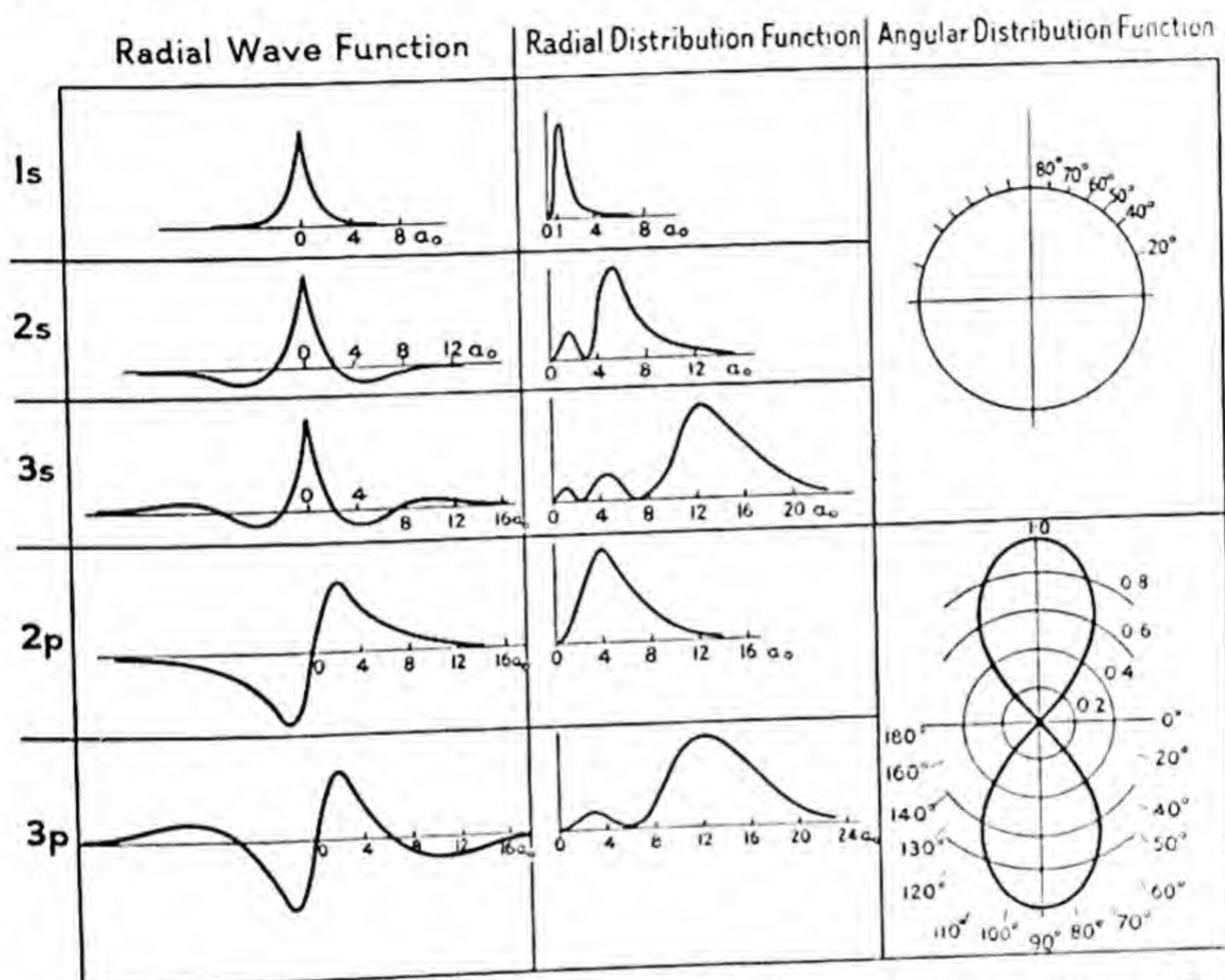


FIG. 2.—The form of (i) the solution of the *radial wave equation*; (ii) the *radial distribution function* or probability of finding an electron at a distance r from the nucleus; (iii) the *angular distribution function*, or probability of finding an electron along any given radial direction, for s and p electrons of a hydrogen-like atom.

Abcissæ are marked in units of a_0 , the radius of the first Bohr orbit of the hydrogen atom. For states with circular Bohr orbits (*i.e.* $1s$, $2p$, etc.) the maximum of the radial distribution function coincides with the radius of the Bohr orbit.

The model thus described in very general terms applies strictly to the one-electron atom. It may, in principle, be generalized to the heavy, many-electron atoms even though the mathematical difficulties of evaluating the wave functions explicitly may become intractable. We may note two features that have made it particularly fruitful in developing a theory of the chemical bond. Firstly, that the electron is not rigorously localized, but that there

is a finite probability of finding it in an element of space other than its most probable orbit; and secondly, that the electron density distribution of p and d electrons—which may be involved in bonding with most elements other than hydrogen—is inherently *directed* in space. The relevance of these features will be apparent in a later chapter.

CHAPTER II

ATOMIC WEIGHTS AND ISOTOPES

In Dalton's formulation of the atomic theory, the relative weights of the atoms were regarded as being the most characteristic and fundamental property of the elements. The chemical properties of an element are directly determined, however, not by its atomic weight but by the number and arrangement of the circumnuclear electrons. These, in turn, must necessarily be numerically equivalent to the nett nuclear charge, or atomic number, of the element. The atomic number thus replaces the atomic weight as being the primary characteristic of each element, and the existence of atoms, differing in mass, but with the same nett nuclear charge and therefore identical chemical properties, at once becomes conceivable.

The recognition that such *isotopes* could exist was first forced upon chemists from the study of the radioactive elements. It has since been shown, largely as a result of the pioneer work of J. J. Thomson and F. W. Aston, that the stable elements are also made up of mixtures of isotopic species, and that very few of the elements, indeed, are simple (see Table 1). Our knowledge of the existence of isotopes of the stable elements is derived from the evidence provided by the mass spectrograph,¹ and from the study of band spectra.

The operation of the mass spectrograph is based on the deflexion of electrically charged atoms or molecular fragments in an electrical or magnetic field. The element to be examined is made to form ions, which, after collimation to a suitable beam, are subjected to the action of measured electrical and magnetic fields. The ions are thereby deflected, the magnitude of the deflexion being a function of the ratio e/m of the charge of the ion to its mass. The ions may be formed by a discharge through the vapour of some volatile compound, by evaporation from a coated hot filament, or by the method of anode rays. The effects of the electrical and magnetic fields may be crossed, so that particles having the same e/m fall on a parabolic curve, or applied in the same direction so

¹ F. W. Aston, 'Mass Spectra and Isotopes', Arnold & Co., London, 1933; *Proc. Roy. Soc.*, 1927, A, 115, 487. For the methods of Dempster, Bainbridge, *et al.*, see Aston, *op. cit.*, pp. 83, 88.

as to exert a focusing effect, whereby particles of the same e/m are concentrated into an image of the slit system. The latter method especially has given results of great value.

When a beam of positive rays, formed from a complex element (*i.e.* one consisting of several isotopes), is subjected to the action of the electrical and magnetic fields, each nuclear species, having some definite nuclear mass m , is registered separately on the photographic plate. By 'bracketing' the observed mass lines between those of known ions, the relative masses of the isotopes of many elements have been compared with great precision. In his second mass spectrograph,² Aston achieved an accuracy of 1 part in 10,000 in the measurement of isotopic masses.

An alternative method of studying isotopes, especially in the case of the lighter elements, is based on spectroscopic measurements. The absorption (or emission) spectra of molecules are complex, and are produced by

- (a) changes in the rotational energy of the molecule, giving rise to an absorption spectrum in the far infra-red ;
- (b) changes in the vibrational energy of the molecule, which—in combination with simultaneous changes in the rotational energy—give rise to absorption bands in the near infra-red ;
- (c) electronic transitions, combined with changes in both vibrational and rotational energy, which produce a band spectrum in the visible or ultra-violet region.

The rotational and vibrational energies of a molecule involve the moment of inertia and the reduced mass of the vibrating atoms, respectively. Both of these are therefore functions of the masses of the atoms concerned, and as such will be modified if one kind of atom be replaced by its isotope of different mass. The result will be a small displacement of the rotational and vibrational lines, from which isotopic masses may be calculated.

Notable examples of the success of the optical method are provided by the discovery of the isotopy of oxygen, carbon and nitrogen. The absorption bands of oxygen showed a series of rotational lines which Giauque and Johnston³ were able to account for quantitatively by attributing them to a molecule, which may be formulated $O^{16}O^{18}$, formed by the union of one oxygen atom of mass 16 with an oxygen atom of mass 18 ; a second, much fainter set of lines was due to a molecule $O^{16}O^{17}$. The existence of isotopes of oxygen with masses 18 and 17, respectively, which had not been revealed by the mass spectrograph, was thereby established. The heavy oxygen isotopes are relatively rare, the proportions being of

² *Proc. Roy. Soc.*, 1927, A, 115, 487.

³ *Nature*, 1929, 123, 318, 831 ; *J. Amer. Chem. Soc.*, 1929, 51, 1436.

the order $O^{16} : O^{18} = 600 : 1$; $O^{18} : O^{17} = 5 : 1$. In a similar way, the so-called Swan bands in the flame spectrum of burning hydrocarbons, which are produced by a transient C_2 molecule, revealed the existence of an isotope C^{13} , present to the extent of about 1 per cent.⁴ Naudé,⁵ in an examination of the absorption spectrum of nitric oxide, likewise found absorption bands due to a molecule $N^{15}O^{16}$, in addition to those of $N^{14}O^{16}$, $N^{14}O^{17}$ and $N^{14}O^{18}$. In all these cases, the existence of the rare isotope had not been shown by the mass spectrograph, owing in large measure, probably, to the existence of more abundant molecular fragments of nearly the same mass. Thus, H_2O and HO , invariably present in the discharge, have about the same masses as O^{18} and O^{17} ; $C^{12}H$ has nearly the same mass as C^{13} . Only in the case of hydrogen is the isotope effect in the atomic line spectrum sufficient to afford a ready means of detecting isotopy. Deuterium was detected spectroscopically in this manner.⁶

In Table 1 are summarized the data at present available as to the isotopic constitution of the elements. Certain features at once stand out from an examination of the figures, shedding some light on the important problem of the structure of the atomic nucleus.

(a) The mass of a stable nucleus is (except for H^1 and He^3) never less than twice its atomic number. On current views, it is built up of protons and particles of unit mass and zero charge, termed neutrons. Hence there are always at least as many neutrons in the nucleus as there are protons.

(b) The number of neutrons in the nucleus tends to be even. In general, the isotopes of elements of odd atomic number have odd mass numbers, whereas the most abundant isotopes of the even elements are, in nearly all cases, those of even mass.

(c) In only two cases—hydrogen and potassium—have elements of odd atomic number been found to possess more than two isotopes. Of these exceptions, the third isotope of hydrogen, H^3 or tritium, does not occur naturally, while the rarest of the potassium isotopes, K^{40} , is probably responsible for the radioactivity of potassium, and thus constitutes an unstable species. Where an element of odd atomic number consists of two isotopes, these invariably differ in mass number by two units, in accordance with (b) above.

(d) The elements of even atomic number are, for the most part, much more abundant in nature than are the odd elements.

⁴ King and Birge, *Nature*, 1929, 124, 182.

⁵ *Phys. Rev.*, 1929, [ii], 34, 1498; 1930, 35, 130; 36, 333.

⁶ Urey, Brickwedde and Murphy, *ibid.*, 1932, [ii], 40, 1; see p. 267,

Table 1
*Isotopic Composition of the Elements **

<i>Element</i>	<i>Atomic number</i>	<i>Stable isotopes, in order of abundance</i>	<i>Element</i>	<i>Atomic number</i>	<i>Stable isotopes, in order of abundance</i>
H	1	1, 2	Sn	50	120, 118, 116, 119, 117, 124, 122, 112, 114, 115
He	2	4, 3	Sb	51	121, 123
Li	3	7, 6	Te	52	130, 128, 126, 125, 124, 122, 123, 120
Be	4	9	I	53	127
B	5	11, 10	Xe	54	129, 132, 131, 134, 136, 130, 128, 126, 124
C	6	12, 13	Cs	55	133
N	7	14, 15	Ba	56	138, 137, 136, 135, 134, 130, 132
O	8	16, 18, 17	La	57	139
F	9	19	Ce	58	140, 142, 138, 136
Ne	10	20, 22, 21	Pr	59	141
Na	11	23	Nd	60	142, 144, 146, 143, 145, 148, 150
Mg	12	24, 25, 26	Pm	61	None
Al	13	27	Sm	62	152, 154, 147, 149, 148, 150, 144
Si	14	28, 29, 30	Eu	63	151, 153
P	15	31	Gd	64	158, 160, 156, 157, 155, 154, 152
S	16	32, 34, 33	Tb	65	159
Cl	17	35, 37	Dy	66	164, 162, 163, 161, 160, 158
A	18	40, 36, 38	Ho	67	165
K	19	39, 41, 40	Er	68	166, 168, 167, 170, 164, 162
Ca	20	40, 44, 42, 43, 48, 46	Tm	69	169
Sc	21	45	Yb	70	174, 172, 173, 171, 176, 170, 168
Ti	22	48, 46, 47, 50, 49	Lu	71	175, 176
V	23	51	Hf	72	180, 178, 177, 179, 176, 174
Cr	24	52, 53, 50, 54	Ta	73	181
Mn	25	55		74	184, 186, 182, 183, 180
Fe	26	56, 54, 57, 58	Re	75	187, 185
Co	27	59	Os	76	192, 190, 189, 188, 186, 187, 184
Ni	28	58, 60, 62, 61, 64	Ir	77	193, 191
Cu	29	63, 65	Pt	78	195, 194, 196, 198, 192
Zn	30	64, 66, 68, 67, 70	Au	79	197
Ga	31	69, 71	Hg	80	202, 200, 199, 201, 198, 204, 196
Ge	32	74, 72, 70, 73, 76	Tl	81	205, 203
As	33	75	Pb	82	208, 206, 207, 204
Se	34	80, 78, 76, 82, 77, 74	Bi	83	209
Br	35	79, 81	Th	90	232
Kr	36	84, 86, 82, 83, 80	U	92	238, 235
Rb	37	85, 87			
Sr	38	88, 86, 87, 84			
Y	39	89			
Zr	40	90, 91, 91, 93			
Nb	41	93			
Mo	42	98, 96, 95, 92, 97, 94, 100			
Tc	43	None			
Ru	44	102, 104, 101, 99, 100, 96, 98			
Rh	45	103			
Pd	46	106, 108, 105, 110, 104, 102			
Ag	47	107, 109			
Cd	48	114, 112, 110, 111, 113, 116, 106, 108			
In	49	115, 113			

* The naturally occurring, but radioactive isotopes of potassium and rubidium are included.

The Whole Number Rule and Packing Fractions.—One of the earliest results emerging from the discovery of the isotopy of the stable elements was that the relative masses of the various nuclear species, on the scale $O = 16$, were found to be very close to whole numbers. Prout's old conception—that the elements were formed by the aggregation of hydrogen, and therefore that their atomic weights should be whole numbers—had been abandoned as a result of the work of Stas and others, which showed that many atomic weights, when determined accurately, were not integers. On the discovery of isotopes it became clear that the atomic weight of an element is only the weighted mean of the masses of its constituent isotopes, and that these nuclear masses were approximate multiples of the mass of a proton. The idea that atomic nuclei were built up of common structural units—protons and neutrons—once more became reasonable.

More accurate measurements of isotopic masses in the mass spectrograph revealed that the whole-number rule is not strictly correct. The isotopic mass deviates, in general, from the nearest whole number by a small amount, and the magnitude of this divergence may be correlated with the stability of the nucleus. The masses of protons and neutrons, combined together in atomic nuclei, are not strictly additive; a part of their mass is converted into energy, and represents the exothermic energy of formation of the nucleus. The greater the stability of the nucleus, the more energy must be released in its formation, and the greater will be the corresponding mass defect. A study of the divergence of isotopic masses from the whole-number rule therefore provides some direct measure of the relative stability of the elements.

The equivalence between mass (M) and energy (E) is given by the Einstein equation $E = Mc^2$, where c is the velocity of light (2.99776×10^{10} cm. per sec.). The difference between the mass of a nucleus and that of its constituent particles is termed the binding energy of the nucleus. The respective masses of the proton and neutron are 1.00812 and 1.00893. Taking as an example the He^4 nucleus which has a mass of 4.00390, the sum of the masses of the constituent particles is $(2 \times 1.00812 + 2 \times 1.00893)$, or 4.03410, and the binding energy is consequently 0.03020 mass units or 28.12 Mev.⁷ This gives a binding energy per particle of about 7 Mev. A value of roughly 6–9 Mev is found throughout the table of elements, the maximum of 8.7 Mev being found at mass of about 55, *i.e.* for the elements near iron.

⁷ An electron volt is the energy needed to raise an electron through a potential of one volt. The million electron volt unit (Mev.), equivalent to 1.602×10^{-6} erg., is in common use. One mass unit = 931 Mev.

More convenient for consideration than the absolute departure of the isotopic mass from the whole-number rule is the quantity termed by Aston the packing fraction. This is the fractional divergence—*i.e.* the difference between the isotopic mass and the nearest whole number, divided by the isotopic mass. It represents the average gain or loss in mass per unit of mass in the atom in question, as compared with the state of nuclear packing in oxygen. Thus, the mass of the Ni^{58} isotope is given as 57.942. The mass defect is therefore 0.058 units, and the packing fraction is thus

$$\frac{-0.058}{58} = -10 \times 10^{-4}$$

The packing fractions of the elements, when plotted against their mass numbers, lie on a smooth curve (Fig. 3). The numerical

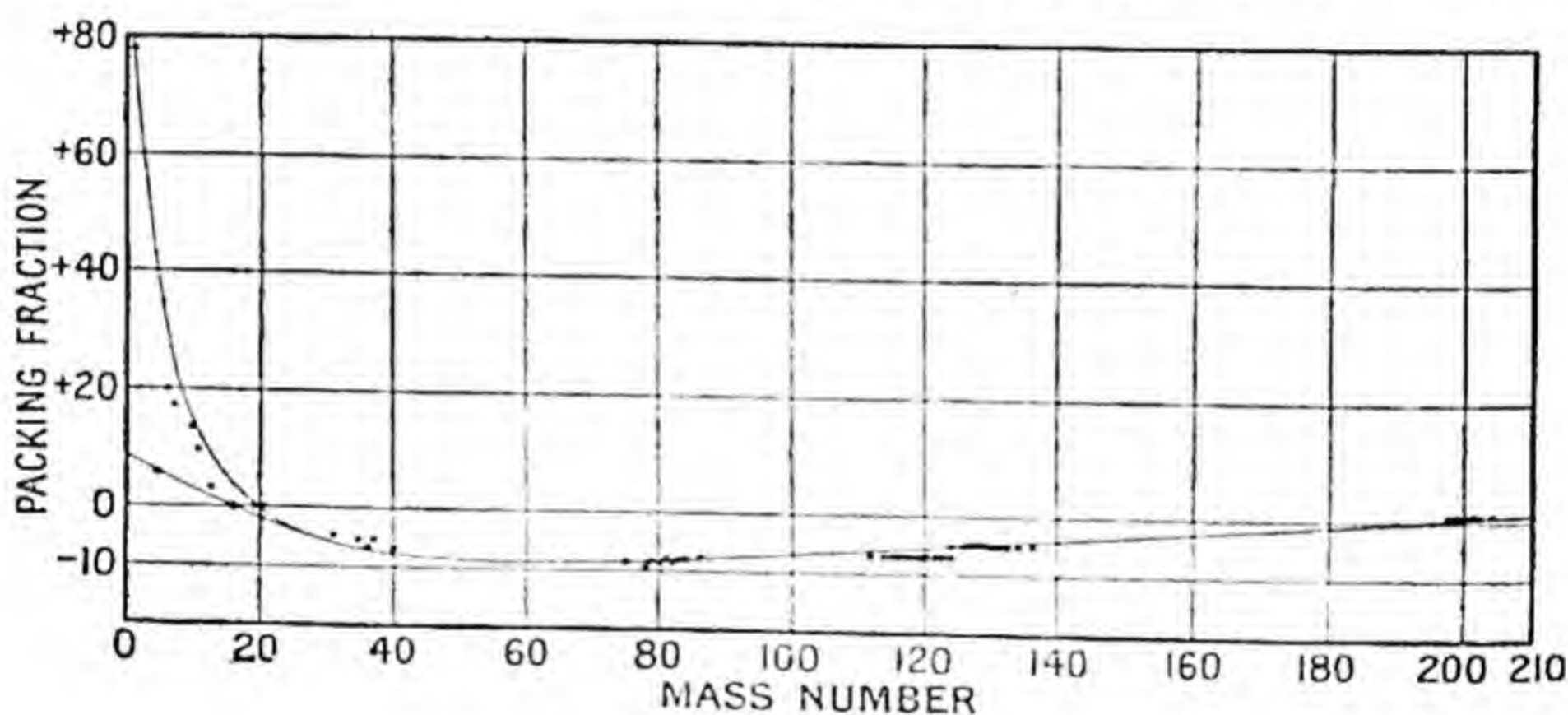


FIG. 3.

values fall from hydrogen ($+78 \times 10^{-4}$) to zero at mass 16–19, and then to a minimum (-10×10^{-4}) in the neighbourhood of mass 50—*i.e.* for the nuclei of iron, nickel, etc. The curve then rises, and the packing fraction once more becomes positive for elements heavier than mercury. The minimum in the packing fraction curve near the atomic mass of iron represents a maximum of nuclear stability. This point is of special interest because of the great preponderance of iron and nickel in the interior of the earth. Nuclear transformations, which are discussed more fully in Chapter XVIII, result in the elimination of matter which is converted into the energy of the nuclear reaction. This point is probably best illustrated by the phenomenon of nuclear fission (see p. 533). The packing fraction curve is used in calculating the accurate mass numbers of isotopes for which precision measurements are not avail-

able. Such data are required for the computation of physical atomic weights.

The Separation of Isotopes.—The problem of separating the isotopes of elements is one which has now assumed a considerable importance for both the physicist and the chemist. The physicist is primarily interested in the nuclear properties of separated isotopes, whereas the chemist's interest centres on the applications of separated or enriched isotopes as tracers in the study of chemical reactions. The theoretical and practical problems involved in the actual separation processes are also of the greatest general interest.

Methods for separating isotopes now in use depend on differences in either the physical or the chemical properties of the isotopes, or of compounds containing them. They arise from differences in internal energy associated with isotopic species. The point may be illustrated by the particular case of the vibrational energy of a chemical bond which depends on the masses of the atoms concerned. There is a difference in the so-called zero-point energy for the bonds involving two isotopic species,⁸ which leads to differences in chemical reactivity and physical properties between isotopic molecules of the same compound (*e.g.* H_2O and D_2O). Effects due to isotopy are greatest among the lighter elements, where relative differences in mass are greater.

Separation by Fractional Distillation.—One of the earliest successful applications of fractional distillation in isotope separation was the partial enrichment of the mercury isotopes by Brönsted and Hevesy,⁹ using the principle of 'ideal distillation'.

A quantity of mercury was distilled at $40\text{--}60^\circ$ in the vessel shown in Fig. 4. The inner vessel was cooled with liquid air and the pressure in the enclosed space was sufficiently low for the mean free path of mercury atoms leaving the surface to be greater than the

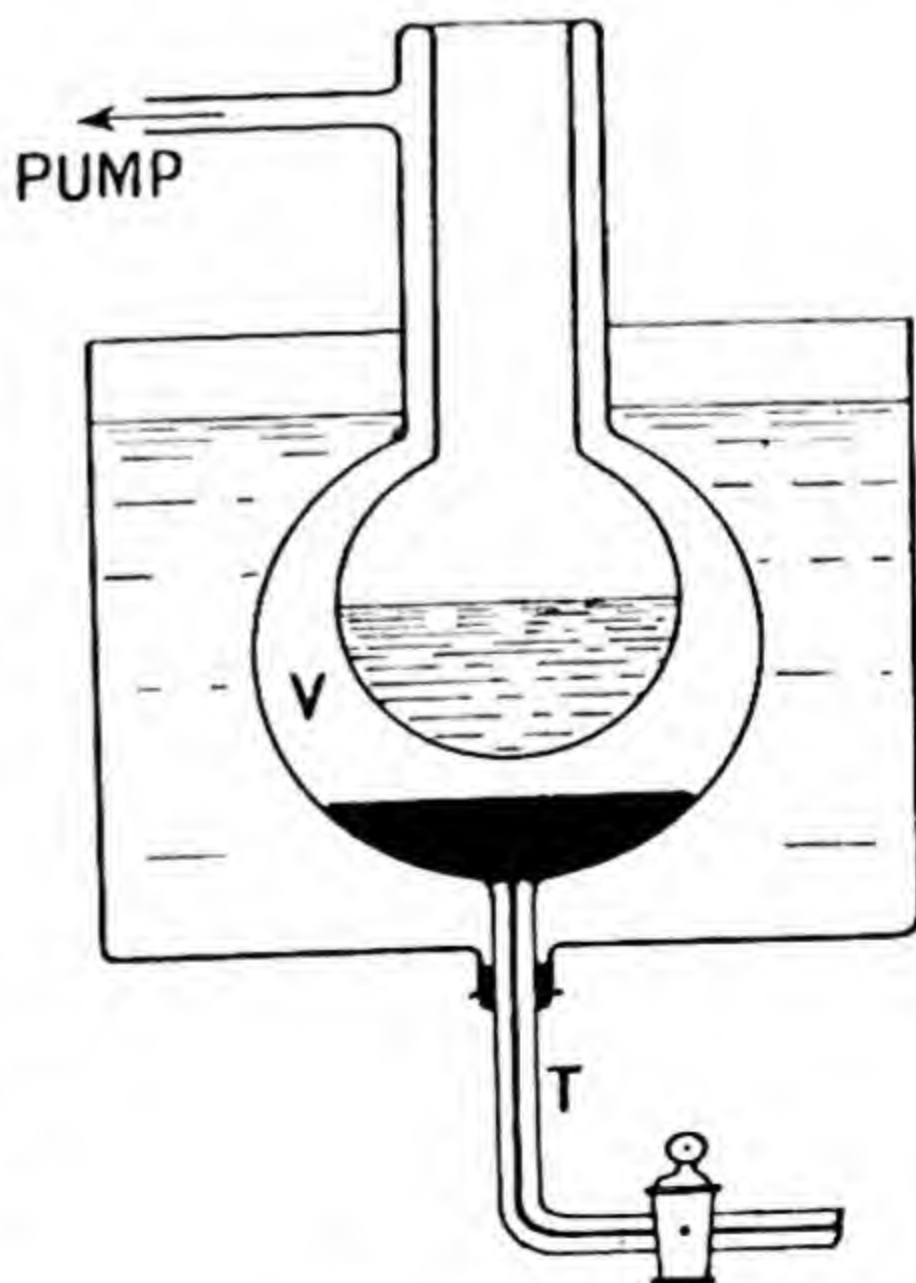


FIG. 4.

⁸ For a review of the effect of isotopy on thermodynamic properties see Urey, *J.C.S.*, 1947, 562.

⁹ *Phil. Mag.*, 1922, 43, 31.

distance to the cold surface. Under these conditions all the atoms which evaporated were condensed, and the condensate was slightly enriched in the more volatile lighter mercury isotopes. When about one fourth of the mercury had evaporated the condensate and residue were separated and systematically refractionated to give small heavy and light fractions with as high an enrichment as possible. From an initial volume of 2700 c.c. of mercury the following results were obtained :

			<i>Relative density</i>	<i>Atomic weight</i>
Lightest fraction	. . .	0.2 c.c.	0.99974	
Light fraction	. . .	2.3 c.c.	0.999824	200.564 ± 0.006
Normal mercury	. . .		1.000000	200.610 ± 0.006
Heavy fraction	. . .	1.1 c.c.	1.000164	200.632 ± 0.007
Heaviest fraction	. . .	0.2 c.c.	1.00023	

For the lighter elements and their compounds differences in vapour pressure for isotopic species are sufficiently great for useful separations to be obtained by the use of efficient fractionating columns. Liquid hydrogen, for example, may be fractionally distilled near its triple point and an enrichment of the deuterium content up to 3 per cent has been obtained in this way.¹⁰ Similarly, the fractional distillation of liquid neon, which normally contains the isotopes Ne^{20} and Ne^{22} in a ratio of about 10 : 1 and has an atomic weight of 20.18, has given a product of atomic weight of 21.16.¹¹ Similar principles have been used in the fractional distillation of water to obtain enrichment of deuterium and of the heavy oxygen isotope O^{18} .

Separation by Fractional Diffusion.—The separation of gaseous molecules of different weight by fractional diffusion is directly dependent on Graham's law, according to which the relative rate of diffusion of two molecular species M_l and M_h is given by the ratio $(M_h/M_l)^{1/2}$. The first application of this principle to isotope separation was due to Aston, who obtained a slight separation of the neon isotopes. Harkins,¹² working with hydrogen chloride at atmospheric pressure, also produced a small separation of the chlorine isotopes. After a laborious series of experiments, chlorine of atomic weight 35.498 was obtained, compared with the normal value of 35.457.

The Harkins method of diffusion at atmospheric pressure is less suited for effective separation than is diffusion at low pressure,

¹⁰ Keesom, van Dijk and Haantjes, *Proc. K. Akad. Wetensch.*, Amsterdam, 1933, 36, 248.

¹¹ Keesom and van Dijk, *ibid.*, 1931, 34, 42.

¹² *J. Amer. Chem. Soc.*, 1921, 43, 1803.

where the Rayleigh diffusion theory applies. According to this, with apertures in the diffusion membrane small compared with the mean free path of the gaseous molecules, the actual enrichment (r) of the heavier component (M_h) of a mixture is given by:

$$r = \frac{M_h + M_l}{M_h - M_l} \sqrt{\frac{\text{Initial volume}}{\text{Final volume}}}$$

With the neon isotopes 20 and 22, for example, the enrichment involves the 21st root of the 'cut', while for the separation of HBr^{79} and HBr^{81} , the 80th root of the cut would be involved.

Fractional diffusion at reduced pressure was first applied successfully by Hertz,¹³ who used a number of porous diffusion units in

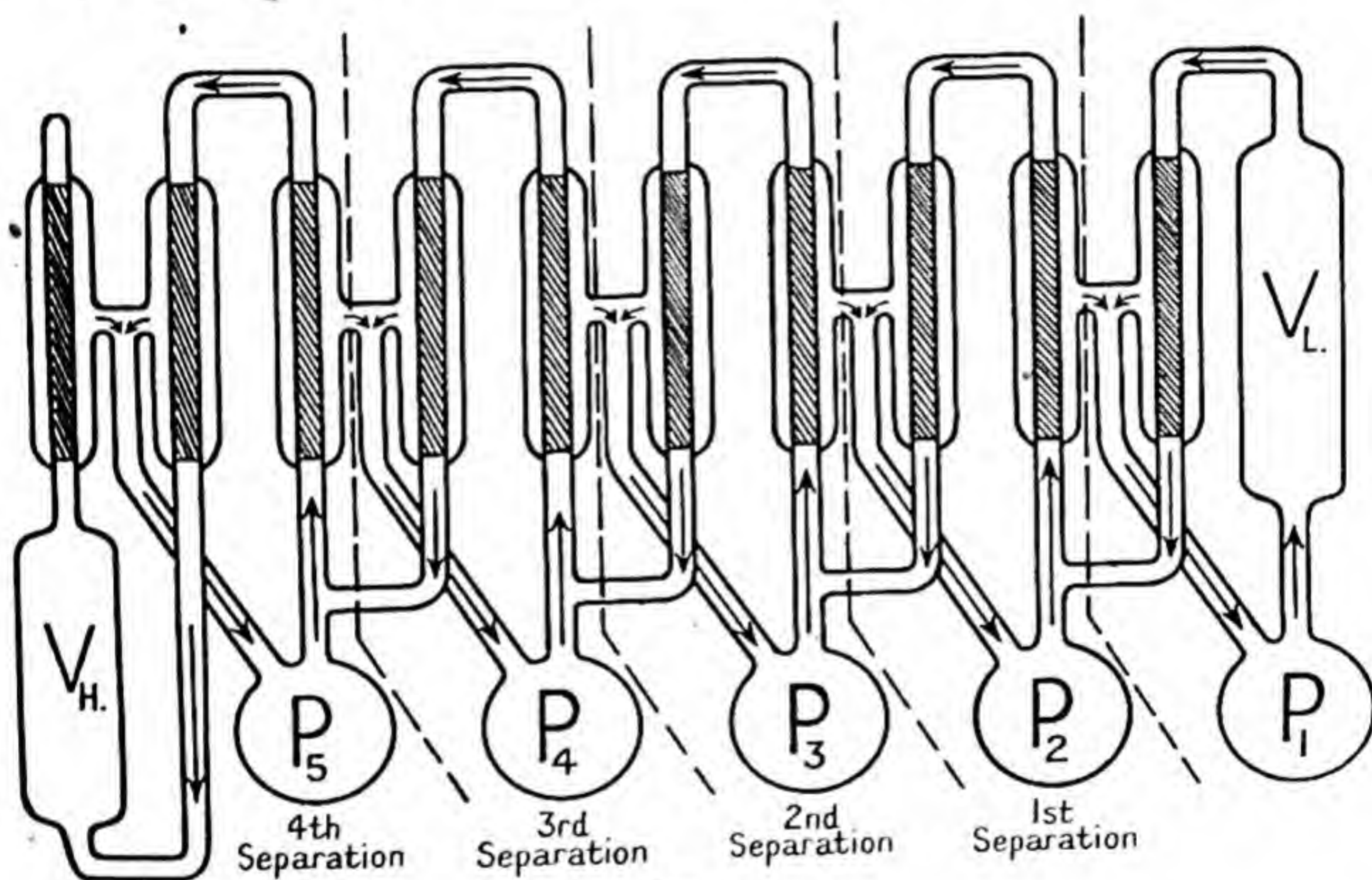


FIG. 5.

series (Fig. 5), mercury diffusion pumps ($P_1 - P_5$) being incorporated in the apparatus to circulate the gas. In each of the diffusion sections, shown by a shaded area in the diagram, there was a small enrichment of the lighter component in the gas passing through the porous membrane, and the direction of circulation was such that the lighter component accumulated in the reservoir on the right and the heavier on the left.

After a period of operation an equilibrium condition is reached. The total separation factor increases exponentially with the number of units, so that in principle any desired degree of separation may

¹³ *Z. Physik*, 1932, 79, 108; 1934, 91, 810.

be obtained by increasing the number of units. Hertz applied a twenty-four unit apparatus of this type to the fractionation of neon, which normally contains Ne^{20} and Ne^{22} in a 10:1 ratio. After eight hours' operation the lighter fraction, occupying 30 litres at 10 mm. pressure, contained less than 1 per cent of Ne^{22} , while in the heavy fraction (400 c.c. at 7.5 mm. pressure) the $\text{Ne}^{20} : \text{Ne}^{22}$ ratio was 2:5. The method has also been applied for the complete separation of hydrogen and deuterium, the enrichment of N^{15} in nitrogen, the enrichment of C^{13} in methane, and for the partial separation of the argon isotopes. Recently the same principle has been used on a technical scale for the separation of the uranium isotopes by the fractional diffusion of the U^{235}F_6 and U^{238}F_6 present in uranium hexafluoride prepared from natural uranium. In this case the lighter isotope is present to the extent of 0.7 per cent. Fluorine has only a single isotope, F^{19} , so that the separation is not complicated on this account.

Separation by Thermal Diffusion.¹⁴—Useful separations of gaseous mixtures may also be obtained by thermal diffusion. If a mixture of light and heavy gaseous molecules is confined in a

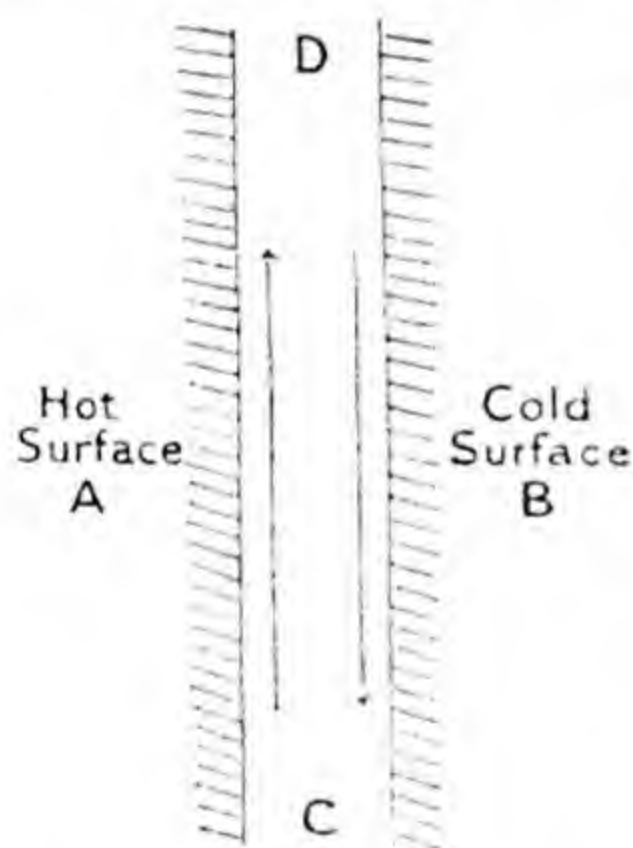


FIG. 6.

space between two surfaces at different temperatures, the heavy molecules tend to diffuse towards the region of lower temperature, and the light molecules towards the region of higher temperature. This effect is independent of ordinary diffusion, which tends to restore a uniform concentration in the gas. If the two surfaces are arranged as shown in the figure, the light component, which is enriched at the surface *A*, will be carried upwards by convection to *D*, and the heavy component will similarly be carried downwards to *C*. If the distance *CD* is relatively large compared with *AB*, ordinary diffusion will clearly exert only

a small effect in restoring a uniform concentration.

This principle was applied by Clusius and Dickel.¹⁵ The apparatus used was a vertical tube of up to 3 m. in length and 1 cm. in diameter, cooled by water on the outside and with a heated platinum wire stretched axially along the tube. Definite separa-

¹⁴ For a more comprehensive review of this topic see Welch, *Chem. Soc. Ann. Repts.*, 1940, 37, 153. An indication of the theoretical basis of thermal diffusion is given.

¹⁵ *Naturwiss.*, 1938, 26, 546.

tions of both the neon and the chlorine isotopes were observed with a temperature difference of 600° between the wire and the outer surface. In order to obtain much greater separations several such columns, each 6–9 m. in length and arranged in series, were used.¹⁶ The bottom of each unit was connected to the top of the next by a closed loop of tubing heated electrically on one side in order to set up convection currents and so mix the gas in the joined ends of the two diffusion units. With such an arrangement HCl^{35} and HCl^{37} were separated almost completely and in useful quantities. The method has also been applied successfully to the separation of the heavy carbon isotope C^{13} , using methane as a carrier gas, the heavy nitrogen isotope N^{15} , and other gaseous mixtures. The apparatus is readily constructed and needs little attention. It may also be operated with a feed of normal material and made to yield a regular take-off of the enriched product required. The method of thermal diffusion has also been applied to pure liquids and solutions, though in general the separations in these cases are smaller.

Other Physical Methods of Isotope Separation.—The electrochemical separation of isotopes is used in the preparation of pure deuterium (*see* p. 266). There is at the same time a small enrichment of the heavy oxygen isotopes. Marked separations of the lithium isotopes have also been obtained, based on the fact that Li^6 is deposited preferentially with respect to Li^7 at a mercury cathode.¹⁷ There is, however, no indication that isotopes of the heavier elements can be separated to any useful extent on the basis of differences in electrochemical behaviour.

The mass spectrograph offers an ideal approach to the problem of isotope separation. The quantities of material which laboratory forms of the instrument could furnish would, however, be extremely small. Recently the principle of the mass spectrograph has been used on a technical scale for the separation of the uranium isotopes U^{235} and U^{238} ,¹⁸ and the same installations could also be used to give at least gram quantities of the separated isotopes of a wide range of other elements. A third separation method which clearly has possibilities of further development depends on the use of the high speed centrifuge,¹⁹ though, taking an overall view of the availability of enriched stable isotopes and also of radioactive isotopes,

¹⁶ *Z. physikal. Chem.*, 1939, B, 44, 451.

¹⁷ Taylor and Urey, *J. Chem. Phys.*, 1937, 5, 597; Holleck, *Z. Elektrochem.*, 1938, 44, 111. *See also* Lewis and Macdonald, *J. Amer. Chem. Soc.*, 1936, 58, 2519.

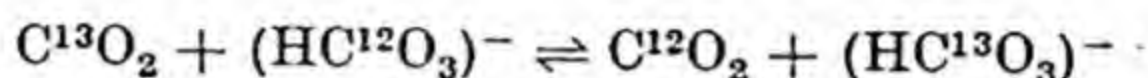
¹⁸ Smyth, 'Atomic Energy for Military Purposes' (Princeton University Press, 1945), p. 195.

¹⁹ *See* Beams and Haynes, *Phys. Rev.*, 1936, 50, 491; Beams and Masket, *ibid.*, 1937, 51, 384; Beams and Snoddy, *J. Chem. Phys.*, 1937, 5, 993.

it seems doubtful if this method will provide materials for research which are not more readily obtained by some other method.

Separation by Chemical Exchange Methods.—It has been found theoretically that there are small differences in the chemical properties of isotopic compounds, which, for the lighter elements, are sufficiently great to provide a basis for isotope separation.²⁰ The most striking case is that of hydrogen and deuterium, which is discussed elsewhere (p. 266), but for elements such as carbon, nitrogen and sulphur very effective isotope separation methods based on chemical exchange have now been developed.

As an example the exchange reaction between gaseous carbon dioxide and the bicarbonate ion in sodium bicarbonate may be considered :



The equilibrium constant (K) of this reaction is found to be 1.012, *i.e.* if the concentrations of the two ions containing C^{12} are taken as large compared with those for the ions containing C^{13} and therefore constant, the ratio $(\text{HC}^{13}\text{O}_3)^-/(\text{C}^{13}\text{O}_2) = 1.012$, and there will be 1.2 per cent more C^{13} in the bicarbonate solution than in the gas in equilibrium with it. Such equilibrium constants may be calculated from the properties of the individual molecules, determined from molecular spectra. The following are typical values for K .

	K
$\text{N}^{15}\text{H}_3(\text{g}) + (\text{N}^{14}\text{H}_4)^+(\text{sol.}) \rightleftharpoons \text{N}^{14}\text{H}_3(\text{g}) + (\text{N}^{15}\text{H}_4)^+(\text{sol.})$	1.031
$\text{HC}^{12}\text{N}(\text{g}) + (\text{C}^{13}\text{N})^-(\text{sol.}) \rightleftharpoons \text{HC}^{13}\text{N}(\text{g}) + (\text{C}^{12}\text{N})^-(\text{sol.})$	1.026
$\text{HCN}^{14}(\text{g}) + (\text{CN}^{15})^-(\text{sol.}) \rightleftharpoons \text{HCN}^{15}(\text{g}) + (\text{CN}^{14})^-(\text{sol.})$	1.003
$\text{S}^{34}\text{O}_2(\text{g}) + (\text{HS}^{32}\text{O}_3)^-(\text{sol.}) \rightleftharpoons \text{S}^{32}\text{O}_2(\text{g}) + (\text{HS}^{34}\text{O}_3)^-(\text{sol.})$	1.019
$\text{S}^{36}\text{O}_2(\text{g}) + (\text{HS}^{32}\text{O}_3)^-(\text{sol.}) \rightleftharpoons \text{S}^{32}\text{O}_2(\text{g}) + (\text{HS}^{36}\text{O}_3)^-(\text{sol.})$	1.040

In using the exchange method to produce enriched isotopes it is first of all necessary to secure conditions such that equilibrium is reached. A multi-stage process is sometimes used, as, for example, in the production of N^{15} by the ammonia-ammonium ion exchange reaction.²¹ A solution of ammonium nitrate is fed into the top of the packed column E (Fig. 7) and $\frac{9}{10}$ of the liquid reaching the bottom passed into a vessel (S), in which ammonia gas is generated by NaOH . This ammonia passes up E . One tenth of the solution reaching the bottom of E passes into the second column E' , at the bottom of which $\frac{9}{10}$ pass into the stripping unit S' for regeneration of ammonia and $\frac{1}{10}$ into E'' , at the bottom of which all the ammonia is regenerated. With such an arrangement, for full details of the

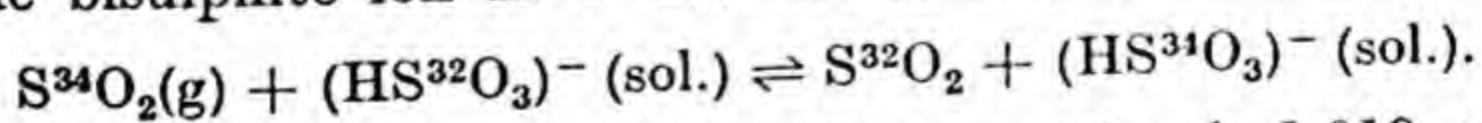
²⁰ Urey and Greiff, *J. Amer. Chem. Soc.*, 1935, 57, 321; Urey, *J.C.S.*, 1947, 562.

²¹ Thode and Urey, *J. Chem. Phys.*, 1939, 7, 34.

operation of which the original paper should be consulted, there is a progressive enrichment in passing from E to E'' ; ammonium nitrate solution with an enrichment of 72.8 per cent of N^{15} could be withdrawn from E'' (the normal nitrogen isotopic ratio being 0.38 per cent N^{15}).

A similar procedure has been used to obtain material enriched in C^{13} , using the exchange between gaseous hydrogen cyanide and sodium cyanide solution.²² This reaction is of interest because it involves both the carbon and the nitrogen isotopes. The isotope C^{13} is concentrated in the gaseous HCN, whereas N^{15} is concentrated to a smaller extent in the liquid phase. Since hydrogen cyanide polymerizes readily and is poisonous the exchange reaction between carbon dioxide and the bicarbonate ion (e.g. in $KHCO_3$) is a more satisfactory way of enriching C^{13} .²³ Enrichment of the heavy isotope occurs in the bicarbonate. A counter current flow method is used and, since equilibrium is reached only slowly at normal pressures, CO_2 pressures up to 50 atm. are employed, together with a packing in the exchange columns of a material such as glass fibre or alumina, which is found to catalyse the reaction. The heavy oxygen isotope O^{18} is enriched in the gas phase in the same reaction.

As a final example of isotope enrichment by means of exchange reactions, the case of sulphur may be considered. The normal isotopic composition is S^{32} , 95.0; S^{33} , 0.74; S^{34} , 4.2; S^{36} , 0.016 per cent. The heavier isotopes may be concentrated with respect to the lighter by means of the exchange reaction between SO_2 gas and the bisulphite ion in a solution of sodium bisulphite:²⁴



The equilibrium constant for the above reaction is 1.019, whereas for the same reaction involving S^{36} it is 1.040. The procedure used is very similar to that in which N^{15} is concentrated in the ammonium

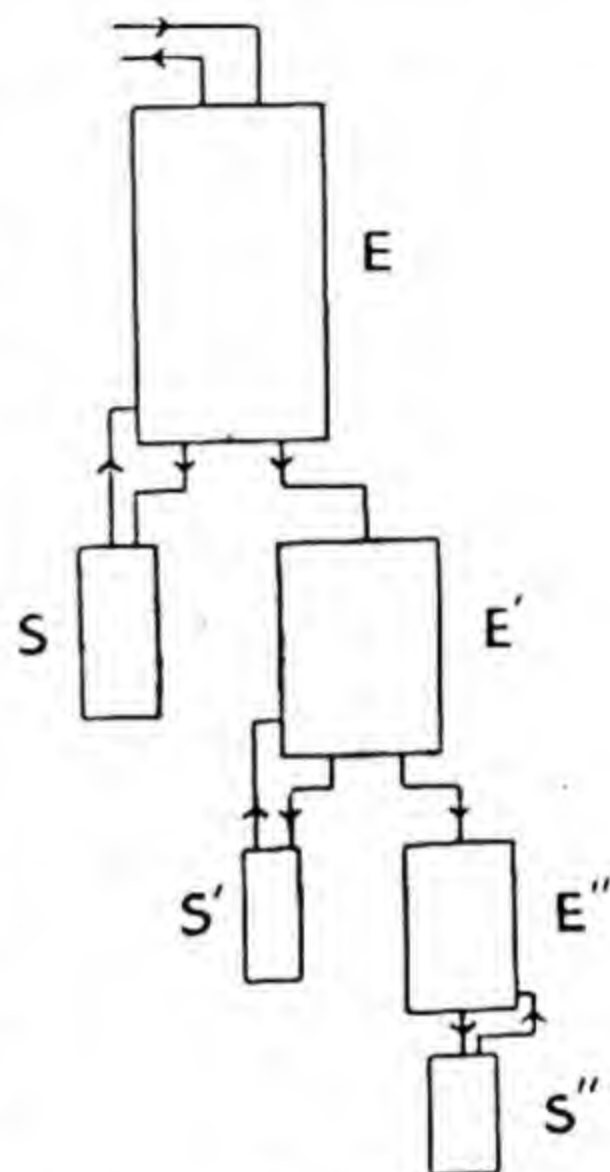


FIG. 7.

²² Roberts, Thode and Urey, *ibid.*, 1939, 7, 137; Hutchinson, Stewart and Urey, *ibid.*, 1940, 8, 532.

²³ Reid and Urey, *ibid.*, 1943, 11, 403.

²⁴ Thode, Gorham and Urey, *ibid.*, 1938, 6, 296; Stewart and Cohen, *ibid.*, 1940, 8, 904.

ion. The method has been used to give concentrates with up to at least 25 per cent of S^{34} .

Applications of Enriched Stable Isotopes.—Enriched stable isotopes are used as tracers in the study of chemical reactions in much the same way as are radioactive isotopes (see p. 541). Typical applications of deuterium are considered later (p. 269). The other stable isotopes which have so far been extensively used are C^{13} , N^{15} , mixtures of O^{17} and O^{18} and mixtures of the heavy isotopes of sulphur. Isotopic assays are made with the mass spectrograph, the degree of enrichment needed in the material used for any particular investigation being governed by the dilution it undergoes in the course of the experiment. The quantities used in the mass-spectrographic assay of an isotopic mixture are small—usually less than 1 c.c. of gas.

The isotope C^{13} is an alternative in tracer studies to the two radioactive isotopes C^{11} and C^{14} . Sulphur enriched in its heavy isotopes has also been used as an alternative to the radioactive isotope S^{35} . There is, however, no radioactive oxygen of suitable half-life and that of N^{13} is also very short ($t_{1/2} = 9.9$ min.). Oxygen and nitrogen enriched in their heavy isotopes therefore assume a special importance in tracer studies.

Most of the work done with N^{15} relates to problems of biological interest, such as those of protein chemistry. As an example of a problem of interest in inorganic chemistry the study of the gas phase exchange reaction



may be cited. This is rapid and may be explained by the intermediate formation of N_2O_3 , the structure of which is symmetrical ($O=N-O-N=O$).²⁵ Another exchange reaction of considerable interest is that between $(N^{14})_2$ and $(N^{15})_2$ on the surface of iron, tungsten and osmium.²⁶ In the case of oxygen some of the most interesting work done concerns the exchange between oxy-anions and the oxygen of water, which has been studied with water enriched in the heavy oxygen isotopes. Thus, for example, there is a rapid and complete oxygen exchange in neutral solution between water and the following anions: SiO_3'' , BO_2' , BO_3''' , Cr_2O_7'' , CrO_4'' , MoO_4'' , WO_4'' , CO_3'' , MnO_4' , IO_3' , SeO_3'' , SO_3'' , S_2O_3'' , AsO_4''' and AsO_2' , but not with NO_2' , ClO_4' , ClO_3' and SeO_4'' .²⁷ It should first be pointed out that no experimental approach other than the use

²⁵ Leifer, *J. Chem. Phys.*, 1940, 8, 301.

²⁶ Joris and Taylor, *ibid.*, 1939, 7, 893; Guyer, Joris and Taylor, *ibid.*, 1941, 9, 287.

²⁷ Winter, Carlton and Briscoe, *J.C.S.*, 1940, 131; Mills, *J. Amer. Chem. Soc.*, 1940, 62, 2833; Hall and Alexander, *ibid.*, 3455.

of isotopic tracer methods could reveal the existence of such exchange reactions. They may be explained in terms of reversible anhydride formation, though it is by no means certain that such a naïve explanation is correct.

The Constancy of Atomic Weights.—The discovery of isotopy immediately raised the question whether the isotopic constitution of the elements is at all variable, or whether it is sensibly constant throughout the universe. In the case of elements derived from many terrestrial sources—for example, chlorine from the sea, or elements from the sedimentary rocks—the known constancy of their atomic weights is to be expected, since the elements as now constituted must have been subjected to the mixing effect of many geological cycles, even if they were originally derived from varying sources. It is of more interest to examine the atomic weight of elements isolated from minerals derived from the primary magma, and from meteorites, which latter afford information as to extra-terrestrial matter.

Various workers have determined the atomic weight of chlorine from primary minerals—*e.g.* sodalite and apatite—and from meteoric sources. In all cases, no difference could be detected between such chlorine and the normal chlorine from sea water. Thus, Harkins and Stone ²⁸ obtained for the atomic weight of chlorine from marine, mineral and meteoric materials the figures given in Table 2.

Table 2

<i>Source</i>					<i>Atomic weight</i>
Salt— <i>i.e.</i> sea water	35.4574
Wernerite	35.4574
Sodalite	35.4580
Apatite	35.4574
Meteorite	35.4580

Similar indications that cosmic and terrestrial elements had identical atomic weights had already been provided by the work of Baxter and Hilton ²⁹ on meteoric nickel, and of Baxter and Thorvaldsen ³⁰ on meteoric iron.

For silicon, also, no deviations from normal isotopic composition were found by Jaeger and Dykstra ³¹ from precise determinations of the density of tetraethyl silane, $\text{Si}(\text{C}_2\text{H}_5)_4$, prepared from silicon

²⁸ *J. Amer. Chem. Soc.*, 1926, 48, 938.

²⁹ *Ibid.*, 1923, 45, 694.

³⁰ *Ibid.*, 1911, 33, 337.

³¹ *Z. anorg. Chem.*, 1925, 143, 233.

derived from six different terrestrial sources and from six meteorites. Boron, however, according to Briscoe and his co-workers,³² shows distinct signs of slight variability. The atomic weight of boron from Tuscan boric acid, Anatolian boracite, and Californian colemanite was determined by the chemical ratio $\text{BCl}_3 : 3\text{Ag}$, and by comparing the density of boron trichloride from the three sources, with the results summarized in Table 3. The atomic weight of Californian boron is perceptibly higher than that of European or Asiatic origin. Since the mass numbers of the isotopes of boron—11 and 10 respectively—are relatively very favourable for fractionation, this apparent difference in isotopic composition may be real.

Table 3

<i>Source of boron</i>	<i>Atomic weight from $\text{BCl}_3 : 3\text{Ag}$</i>	<i>Density of BCl_3</i>	<i>Atomic weight from density</i>
Boric acid, Tuscany . .	10.840 ± 0.014	1.349273	10.823
Boracite, Asia Minor . .	10.819 ± 0.004	1.349213	10.818
Colemanite, California . .	10.840 ± 0.003	1.349478	10.841

The more intensive study of isotopic composition which has followed the discovery of heavy hydrogen has shown that second-order differences in the proportions of isotopes are not infrequently brought about by the chemical separation factor discussed above. In addition to the quite appreciable variations in the proportion of the hydrogen isotopes found by numerous workers,³³ atmospheric oxygen is perceptibly heavier than oxygen combined in natural waters. Water made from atmospheric oxygen is 6.7 parts per million heavier than that made by combining the oxygen of water with the same sample of hydrogen, corresponding to an atomic weight of 16.00012 for atmospheric oxygen.³⁴ An appreciable variation in the ratio of the potassium isotopes has also been reported; according to Brewer,³⁵ the ratio of $\text{K}^{41} : \text{K}^{39}$ is 15 per cent higher in potassium from plant ashes than in potassium from marine salts.

Physical Atomic Weights. Not only the mass numbers but also the abundance of the isotopes may be determined by mass spectrographic analysis. Combination of these data with the packing fractions of the isotopes enables the mean atomic weight of

³² *J.C.S.*, 1925, 696; 1927, 282.

³³ Cf. Briscoe *et al.*, *J.C.S.*, 1934, 1207, 1948.

³⁴ Dole, *J. Chem. Phys.*, 1936, 4, 268.

³⁵ *J. Amer. Chem. Soc.*, 1936, 58, 370.

the isotope mixture to be calculated, independently of any chemical data. It is thus possible to compute a physical atomic weight for many elements, which may be compared with the atomic weight determined chemically.

The direct comparison of physical and chemical atomic weights has been slightly complicated by the discovery that oxygen itself is not a simple element. Chemical atomic weights are measured on the scale, normal oxygen = 16; physical atomic weights are based on comparison with the O^{16} isotope = 16.000. The relation between the two scales involves, therefore, a knowledge of the relative abundance of the isotopes of oxygen—chiefly the $O^{16} : O^{18}$ ratio. This ratio is not yet determined with complete certainty, but probably lies between 630 : 1 (Mecke and Childs ³⁶) and 514 : 1 (Urey, Manian and Bleakney ³⁷). The conversion factor between physical and chemical atomic weights is thus 1.00022 or 1.000275 : 1.

Chemical Atomic Weights and their Basis.—The development of purely physical methods of calculating atomic weights from isotope abundance data has enabled a comparison to be made in many cases with the values determined from chemical ratios. In a number of instances where the physical and chemical values have disagreed, a redetermination of the chemical atomic weight has vindicated the accuracy of the mass spectrographic method.

Although the fundamental importance of the atomic weight as a characteristic of each element has been supplanted by the concept of the atomic number, a knowledge of accurate atomic weights is still essential from the chemical standpoint, and determinations of atomic weight afford, in many cases, a convenient means of studying variations in the isotopic composition of elements from different sources. Concurrently with the physical studies of isotopy, therefore, there has been a considerable body of work in recent years devoted to the accurate revision of atomic weights, and more especially to the precise determination of the fundamental ratios.

The chemical atomic weights are, of course, based on the scale $O = 16$, but in most cases the stoichiometric ratios actually determined necessarily involve elements other than oxygen. Thus, for many elements the halide ratios *metallic halide : silver*, or *metallic halide : silver halide*, are convenient, and susceptible of accurate experimental determination. The calculation of the atomic weight from them presupposes a knowledge of the atomic weight of silver, or of silver and chlorine or bromine, on the oxygen scale. The accepted values of these represent the weighted means obtained by combining a number of independent ratios involving the atomic

³⁶ *Z. Physik*, 1931, 68, 362.

³⁷ *J. Amer. Chem. Soc.*, 1934, 56, 2601.

weights of nitrogen, hydrogen, the halogens, silver, sulphur, carbon and sodium.

The Ag:Cl and Ag:Br ratios are known with considerable precision. In practice, therefore, the atomic weight fundamental for the accuracy of all others is that of silver on the oxygen scale.

In any precision determination of atomic weights three points deserve especial attention: the stoichiometric composition of the compounds used, the quantitative completion of the reaction performed, and the problems of adsorption of air, etc., which are associated with the utmost refinement of accuracy in weighing. It is profitable to study recent work in this field from the standpoint of these requirements. The foundations of the necessary technique were laid by T. W. Richards; the general principles established by him have in recent years been carried yet further, and have resulted in the extremely accurate work of Hönigschmid's school at Munich, in particular.

As illustrating the development of this work, the fundamentally important determination of the atomic weight of silver on the oxygen scale is instructive. There are two general approaches to this problem: the direct measurement of such ratios as $\text{KClO}_3 : \text{KCl} : \text{Ag} : 3\text{O}$, whereby the oxygen in a halogen oxyacid is equated directly to the silver required for reaction with the corresponding halide; and the indirect calculation of the atomic weight of silver from ratios involving the atomic weight of a third element—*e.g.* from the ratio $\text{Ag} : \text{AgNO}_3$, assuming the atomic weight of nitrogen.

Marignac and Stas attempted the direct correlation between oxygen and silver by carrying out the thermal decomposition of the alkali chlorates and bromates. The value $\text{Ag} = 107.93$, accepted for many years, was based largely on this method. The alkali chlorates and bromates are not, however, suited for the purpose of the most accurate determinations. Richards early showed that only those compounds can be brought to a rigorously stoichiometric composition that can be freed from moisture by strong heating—preferably fusion—in a suitable atmosphere; metallic chlorides are thus customarily fused in a stream of dry hydrogen chloride before weighing. Fusion is further desirable in that, by diminishing the surface area of the material, the adsorption of air is greatly diminished. With finely crystalline powders, the latter effect may be more considerable than was formerly supposed.

Of the indirect correlations between silver and oxygen, the work of Richards and Forbes³⁸ on the synthesis of silver nitrate is the most important, as representing the inception of the modern phase

³⁸ Carnegie Inst. Publ., 1907, 69, 47; *Z. anorg. Chem.*, 1907, 55, 34.

of the subject. The evaluation of this ratio requires the assumption of the atomic weight of nitrogen $N = 14.008$, and although this value has recently been fully substantiated by the mass spectrographic method, and is supported, independently of chemical ratios, by gas density determinations, a confirmation of the derived value for silver by some direct silver: oxygen ratio was logically desirable. The position of the atomic weight of silver in 1927 was summarized by Hönigschmid³⁹ in the following table:

(A) Direct Ratios.

Ag : LiCl : LiClO ₄ : 4O	.	.	Ag = 107.871
KClO ₃ : KCl : Ag : 3O	.	.	107.871
I ₂ O ₅ : 2AgI, Ag : I	.	.	107.864

(B) Indirect Ratios.

Ag : AgNO ₃	.	.	.	107.880	Assuming N = 14.008
NaNO ₃ : NaCl : Ag, Ag : AgCl	.	.	.	107.880	N = 14.008
Ag ₂ SO ₄ : 2AgCl : 2Ag, N : S	.	.	.	107.877	N = 14.008
NH ₄ Cl : Ag, AgNO ₃ : Ag, AgCl : Ag	.	.	.	107.881	H = 1.008
2H ₂ O : BaCl ₂ : 2Ag	.	.	.	107.876	H = 1.008

Richards and Willard (1910) attempted to overcome the difficulties inherent in the decomposition of alkali chlorates by converting lithium chloride to the perchlorate. Lithium chloride was evaporated down with perchloric acid in quartz flasks, and the lithium perchlorate so formed was weighed *in situ*. It was not possible, however, to fuse the lithium perchlorate without some decomposition occurring, and the final weight had therefore to be corrected for the presence of traces of chloride and chlorate. As may be seen, this result, when combined with the separately determined ratio Ag : LiCl, gives a distinctly lower atomic weight for silver than the indirect ratios, obtained prior to 1927, which are quoted in section [B] of the table. The same applies to Baxter and Tilley's determination of the I₂O₅ : 2AgI ratio (1909) and to Stähler and Meyer's redetermination of the classical KClO₃ : KCl : Ag ratio (1911).

Hönigschmid and Sachtleben⁴⁰ determined a new direct silver-oxygen ratio—Ba(ClO₄)₂ : BaCl₂ : 2Ag : 8O—which was designed to avoid the sources of error inherent in the previous work. The transference and evaporation of liquids was avoided by the use of the dry reaction with hydrogen chloride gas. It was not possible to fuse barium perchlorate without decomposition, but errors arising from the adsorption of gases on the materials weighed were avoided by carrying out all weighings *in vacuo*. These two features—the

³⁹ *Z. anorg. Chem.*, 1927, 163, 65.

⁴⁰ *Ibid.*, 1929, 178, 1.

use of dry reactions wherever possible, and the elimination of adsorption errors by vacuum weighing—are characteristic of the modern work of the Munich school. Thus, Hönigschmid has completely confirmed the value found by Richards and Forbes for the ratio $\text{Ag} : \text{AgNO}_3$ by the dry reduction of silver nitrate to metallic silver.⁴¹

The method of conducting dry reactions is shown by the work of Hönigschmid and Sachtleben, illustrated by Fig. 8. The barium perchlorate, in the boat *A*, was dried at 260° in a current of purified and dried air. The quartz tube *B* was connected by means of a ground flange to a glass section *C*, and this in turn to the glass tube *D* which served for the transfer of the boat from the reaction tube *B* to the bottling apparatus *E*.⁴² After the completion of the drying, the boat was pushed into *D*, which could then be transferred, in a counter-current of dry air, to the bottling apparatus *E*. This could then be evacuated, and the boat pushed by the magnetically

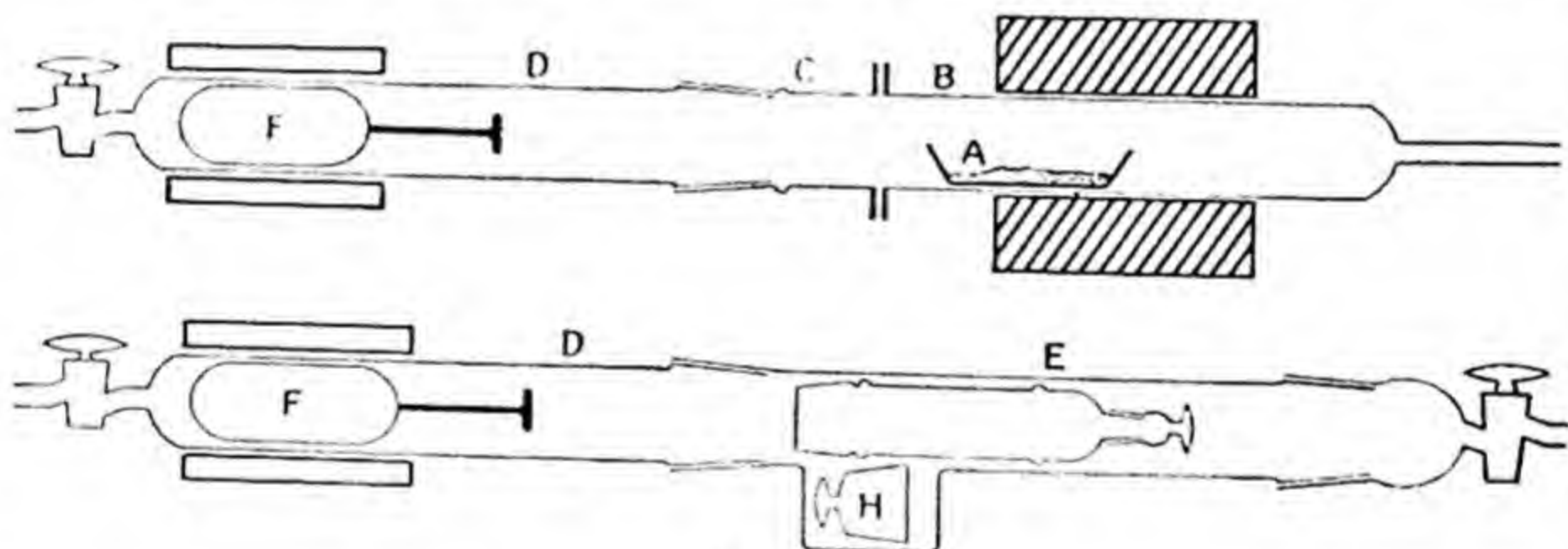


FIG. 8.

operated piston *F* into the weighing-tube. Finally, the bottling apparatus was so rotated that the boat *H* could be pushed into place by means of *F* without breaking the vacuum. By this means, the boat could be transferred from the reaction tube to the vacuum weighing-bottle; it was returned to the reaction tube *B* by a similar set of operations, and heated in a stream of dry hydrogen chloride, first at 200° and finally at 550° , to convert the perchlorate to barium chloride. This in turn was weighed *in vacuo*, and was finally determined with silver in the usual nephelometric manner.

The results of this direct measurement of the ratio $\text{Ag} : 4\text{O}$ agree completely with the atomic weight of silver as determined from the

⁴¹ cf. Hönigschmid, Zintl and Thilo, *Z. anorg. Chem.*, 1927, 163, 65; Hönigschmid and Schlee, *Angew. Chem.*, 1936, 49, 464; Hönigschmid and Striebal, *Z. physikal. Chem.*, Bodenstein Festband, 1931, 283.

⁴² Richards and Parker, *Proc. Amer. Acad.*, 1896, 32, 59.

ratio $\text{Ag} : \text{AgNO}_3$. Their striking concordance is shown by the figures given below.

$\text{Ba}(\text{ClO}_4)_2 : \text{BaCl}_2$	$\text{Ba}(\text{ClO}_4)_2 : 2\text{Ag}$	$\text{Ag} : 4\text{O}$	Atomic weight of Ag
1.61458	1.55856	1.68561	107.879
1.61460	1.55849	1.68565	107.882
1.61459	1.55858	1.68558	107.877
1.61459	1.55850	1.68565	107.882
1.61459	1.55850	1.68566	107.882

It is, indeed, found that the reproducibility attainable in the ratio based on the dry reaction actually exceeds that achieved in the argentometric determination, which involves the still disputed nephelometric endpoint.⁴³ For this reason, the use of dry reactions has been extended to other cases—for example, to the determination of the atomic weights of sulphur and selenium from the ratios $2\text{Ag} : \text{S}$, $2\text{Ag} : \text{Se}$. In each case, the silver compound was synthesized directly from the elements, and the excess of the non-metal was distilled off in a high vacuum. The atomic weight so found for selenium (78.962 ± 0.012) completely confirmed the value computed by Aston from mass spectrographic data (78.96 ± 0.04) which differed considerably from the previously accepted chemical value of 79.2, based chiefly on argentometric ratios.

Atomic Weights from Gas Density Data.—The determination of atomic weights by measurement of gas densities is a method which is especially suitable for those lighter elements—*e.g.* carbon and fluorine—for which suitable chemical ratios, capable of precise determination, are not readily found.

The classical method of gas-density determination, depending on direct weighing, was refined by Rayleigh⁴⁴ and employed since by Leduc, Guye and Moles. More recently, the use of the gas-density microbalance has been developed, especially by Whytlaw-Gray and his collaborators. This instrument, by means of which an accuracy in no way inferior to that of the Rayleigh method is attainable, has certain distinct advantages over the method of direct weighing—*e.g.* in the minimization of adsorption errors, its availability over a wide range of pressures, and its applicability to small quantities. It is therefore worthy of brief comment in this chapter.

The balance, illustrated diagrammatically in Fig. 9, consists essentially of a silica balance beam, *A*, carrying on the one side a buoyancy bulb, *B*, and on the other a counterweight, *C*, the whole turning about a horizontal silica torsion fibre, *D*. The beam balances about the zero only at that pressure of gas at which the

⁴³ Briscoe *et al.*, *Proc. Roy. Soc.*, 1931, A, 133, 440.

⁴⁴ Lord Rayleigh, 'Collected Papers'.

buoyancy effect on the bulb exactly compensates its nett gravitational pull. Since, for different gases at the same pressure, the buoyancy effect is directly proportional to the density of each gas, the determination of gas densities by means of the microbalance reduces to a strictly relative measurement. It requires only the manometric measurement of the balancing pressures for the gas under investigation, and for a standard gas—*e.g.* for pure oxygen, which may thus be used as the direct standard of reference.

Errors due to adsorption, which are of unknown magnitude in the method of direct weighing, can practically be eliminated by so designing the counterweight that its resultant surface moment is equal to and thus counterbalances that of the buoyancy bulb.

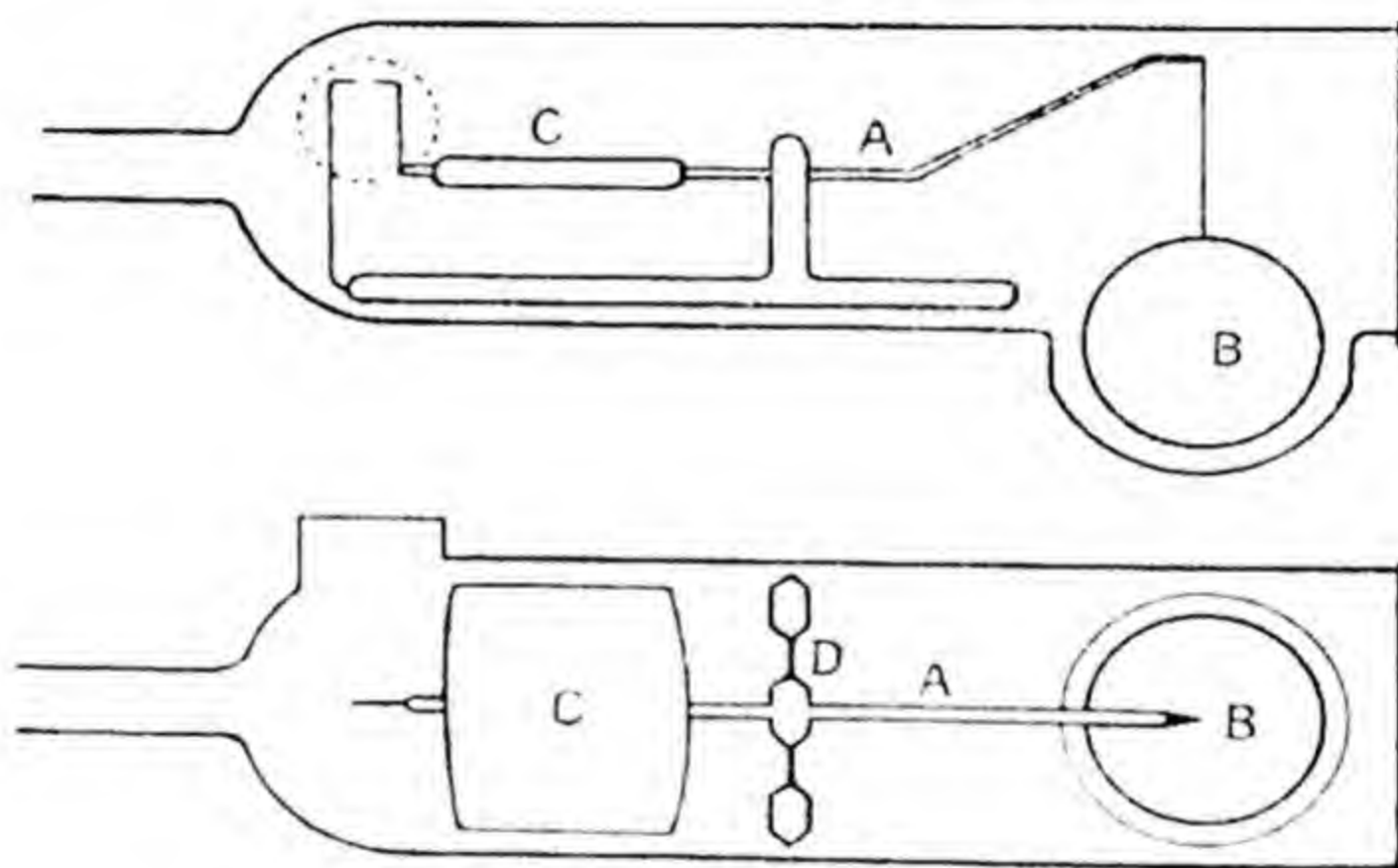


FIG. 9.

By suitably loading the beam, relative density determinations may be made at a number of different pressures; such comparison of densities over a pressure range is of importance, since it eliminates the necessity for the independent determinations of the compressibility of each gas used. The balancing pressures can, in favourable circumstances, be determined to within one part in 100,000, so that the method is capable of giving results of the utmost precision.

Owing to the deviation of real gases from the ideal gas law, the conversion of relative density data to molecular weights involves a knowledge of the compressibility of each gas. At low pressures (of the order of one atmosphere and below), the deviation of practically all gases from the ideal gas law is a linear function of pressure, represented by the Berthelot isotherm

$$pv = p_0v_0(1 - Ap) \quad (A = \text{compressibility}).$$

If, at zero pressure ($= p_0$), the volume of W grams of gas be v_0 c.c., then

$$p_0 v_0 = RT \frac{W}{M}$$

Hence, $pv = RT \frac{W}{M} (1 - Ap)$, and if $\frac{W}{v} = D$, the density of the gas at a pressure p , we have that

$$p = RT \frac{D}{M} (1 - Ap)$$

The microbalance method measures the pressures p_I and p_{II} at which the two gases I and II have the same density. Hence,

$$\frac{p_I}{p_{II}} = r = \frac{M_{II} (1 - A_I p_I)}{M_I (1 - A_{II} p_{II})}$$

or

$$\frac{M_{II}}{M_I} = r \cdot \frac{(1 - A_{II} p_{II})}{(1 - A_I p_I)}$$

The balancing ratio r varies in a linear manner with pressure, and may be extrapolated to its limiting value when $p_I = p_{II} = 0$. From the extrapolated value, r_0 , the ratio of the limiting densities of the two gases, the required molecular weight, M_{II} , is at once obtained. Alternatively, if the compressibility, A_I , of one gas be known, the compressibility, A_{II} , of the second gas may be determined from the values of r at any two pressures, since

$$\frac{r' (1 - A_{II} p'_{II})}{r'' (1 - A_{II} p''_{II})} = \frac{(1 - A_I p'_I)}{(1 - A_I p''_I)}$$

Historically, the use of the gas-density balance for atomic-weight determinations originated in the very elegant work of Whytlaw-Gray and Ramsay on the density of radon,⁴⁵ carried out with an early and undeveloped form of the instrument. Its later use may be illustrated by the redetermination of the atomic weight of carbon,⁴⁶ which has removed a serious anomaly between the hitherto accepted chemical atomic weight and that calculated from physical isotope data. It is perhaps worthy of emphasis that, since gas-density determinations employ normal oxygen as a standard of reference, they give atomic weights on the chemical scale. The atomic weight of carbon accepted up to 1936, $C = 12.00$, which was based largely on the ratio $\text{Na}_2\text{CO}_3 : 2\text{NaBr} : 2\text{Ag}$, was in direct disagreement with the band spectroscopic evidence that carbon

⁴⁵ *Proc. Roy. Soc.*, 1910, A, 84, 536.

⁴⁶ Woodhead and Whytlaw-Gray, *J.C.S.*, 1933, 846; Cawood and Patterson, *Phil. Trans.*, A., 1936, 236, 77. Whytlaw-Gray, *Quart. Rev. Chem. Soc.*, 1950, 4, 153.

contains about one per cent of the C^{13} isotope. Earlier gas-density determinations by Rayleigh, Leduc and Moles, in combination with the available compressibility data, indicated that the chemical atomic weight must be too low. Measurements of the limiting densities of carbon monoxide, carbon dioxide and ethylene with the density balance have vindicated this conclusion, and have given highly concordant evidence for a value close to $C = 12.0108$. This figure is in close agreement with the values derived from mass spectrographic data, and from the energy balances of nuclear processes.

Although the gas-density microbalance, in its most refined form, is an instrument of the precision and sensitivity indicated, it is, nevertheless, essentially a simple and convenient instrument. It may well become an accessory of great utility, with manifold applications in the technique of the manipulation of gases.

CHAPTER III

VALENCY

General relationships between periodicity in chemical properties and periodicity in the atomic structures of the elements will be evident from the discussion given in Chapter I. It should be possible, however, to develop the subject still further by formulating a precise relationship between valency and atomic structure. The goal of such a complete theory would be the prediction of the energies of formation and the detailed molecular structure of all the compounds of the elements. Although such precise theoretical treatment is possible only in a few of the simplest cases, the electronic theory of valency has contributed greatly to an understanding of molecular structure and chemical reactivity, and especially through the development of quantum mechanical theory.¹

Even before the general principles of atomic structure had been fully worked out, the foundations of an electronic theory of valency were laid by Kossel and G. N. Lewis, in 1916, who independently perceived the significance of the inert gases in the Periodic System, as pointing to the stability and special properties of certain complete electronic configurations. Of fundamental importance was Lewis's recognition of two distinct types of chemical bond: the *electrovalent* or ionic bond and the *covalent* bond. Electrovalency involves the transfer of one or more outer electrons from one atom (*e.g.* of a metallic element) to another atom (*e.g.* of a non-metal) with an incomplete outer shell, the two atoms being then bound by the electrostatic attraction of their resultant charges. A covalency arises from the sharing of electrons, two to a bond, between atoms, by a mechanism that has been interpreted only since the development of quantum mechanical theory. If the atoms or groups which are thus joined are not identical, the electrons are, in general, not shared equally, so that the resulting bond has a dipole moment. In the particular type of covalency known as a *coordinate link*, both the shared electrons of the bond are provided by one of the two atoms that are joined together.

¹ The reader is referred especially to C. W. Gurney, *Ions in Solution* (Cambridge University Press), and L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press), for further reading.

Electrovalency.—In inorganic chemistry the electrovalent compounds—the salts—are especially important. It is pertinent to enquire what determines the mode of binding of the elements in any compound and, further, what limits the variability of valency of the elements.

The formation of an electrovalency arises from the special properties of closed electronic shells. Thus, the formation of a sodium ion from a neutral sodium atom leaves the positive ion with two 1s, two 2s and six 2p electrons, a configuration which may be abbreviated as $1s^2 2s^2 2p^6$. Since all orbits of the second quantum level are fully occupied, the resultant orbital angular momentum and the resultant electronic spin angular momentum are both zero, and in consequence the interaction of the electrons with other atoms is a minimum. The inert gas atoms, in which a closed shell is combined with electrical neutrality, are therefore inert; inert-gas-like ions, such as Na^+ , Cl^- , Sr^{++} , exert electrostatic forces in virtue of their nett charge. Although the interaction of closed configurations (other than by electrostatic effects) with other atoms or ions is small, it becomes considerable for very small interatomic distances, comparable with atomic dimensions. The perturbing effect of adjacent ions then modifies the distribution of electron density and distorts, or polarizes, the symmetry of the inert-gas-like ion.

Since cations are, on the whole, smaller than negative ions, they exert a correspondingly greater polarizing effect. The significance of ionic polarization was early realized by Fajans, who showed from measurements of ionic refractivities that the greatest effect was exerted by small cations, of high valency, upon the largest anions. He pointed out that the concept of pure electrostatic forces between spherical ions is an ideal picture, to which real salts deviate to an extent depending on the particular ions concerned. If the polarization effects are sufficiently great, we can conceive of distortion of the anions proceeding so far that the electron systems of the two ions become fused into one; the ionic state will give place to a covalent bond between the atoms.

The trend of ionic sizes, and the progressive changes of valency, make the polarizing power of cations increase markedly from left to right across the Periodic Table, but decrease downwards within any one group. The caesium ion Cs^+ thus has the lowest polarizing power, while that of the small Be^{2+} and Al^{3+} cations is very great. The polarizability of negative ions varies with their valency and their effective size; it is least for the fluorine ion F^- , and greatest for the Te^{2-} and I^- ions. The influence of the polarization effect upon the properties of binary ionic compounds can thus be correlated with the position of the elements in the Periodic System.

Whilst it is true that an inert-gas-like ion represents a stable electronic configuration, and that those elements which have one or two electrons in excess of it or short of it tend to assume this configuration by ionization, the energy balance sheet involved in forming an electrovalency merits examination. The production of a positive ion from a neutral atom involves the expenditure of a considerable amount of energy, since the electrons must be removed against the electrostatic attraction of the remaining positive ion. The *ionization energy*, I_M , in kilocalories per gram atom, for the production of inert-gas-like ions from the isolated atoms of a few metallic elements is listed in Table 1.

Table 1

H ⁺ 311	Li ⁺ 123.8	Na ⁺ 118.0	K ⁺ 99.7	Rb ⁺ 95.9	Cs ⁺ 89.4
	Be ²⁺ 594.5	Mg ²⁺ 520.8	Ca ²⁺ 412.9	Sr ²⁺ 383.7	Ba ²⁺ 348.9
	B ³⁺ 1648	Al ³⁺ 1223	Sc ³⁺ 1019	Y ³⁺ 907	La ³⁺ 831
	Cu ⁺ 177.4	Ag ⁺ 174		Zn ²⁺ 313	Cd ²⁺ 297
	Cu ²⁺ 642				

Neutral atoms which are just short of a closed configuration have a corresponding *electron affinity*, E_X . Thus the process $\text{Cl} + e \rightarrow \text{Cl}^-$ is exothermic to the extent of about 92.5 kilocalories per gram atom. The electron affinities for formation of the ions indicated from the neutral atoms of a few typical non-metals are collected in Table 2.^{1a}

Table 2

H ⁻ + 32.2	F ⁻ + 81.7	Cl ⁻ + 92.5	Br ⁻ + 87.1	I ⁻ + 79.2
	O ⁻ + 29.1	S ⁻ about + 40		
	O ²⁻ - 166	S ²⁻ - 79.5		

This electron affinity arises principally from the coupling of electron spins between the added electron and its partner in an orbit originally only singly occupied; the maximum electrovalency is given by the number of unpaired electron spins. It will, however, be noticed that for the formation of O^{2-} or S^{2-} , the electrostatic repulsion involved in adding the second electron outweighs the energy gain due to coupling of spins, so that the formation of these inert-gas-like ions is actually an endothermic process.

If we consider the formation of an electrovalent bond between a pair of isolated atoms M, X, only a part of the energy of ionization is, in general, supplied by the electron affinity of the non-metal atom X. The nett expenditure of energy is $\Delta H = +I_M - E_X$ as long as the ions remain separated, and except for the formation of the ion pairs Rb^+F^- , Cs^+F^- , Cs^+Cl^- this over-all process would be endothermic. When the ions are brought together, to form a

^{1a} The electron affinity of fluorine, taken from Evans, Warhurst and Whittle, *J.C.S.*, 1950, 1524, is lower than the figures normally assumed.

molecule in the vapour of a binary salt, there is a gain of electrostatic energy, U_r , given by the inverse square law of attraction between them. For such compounds as the halides of the alkali metals the U_r is of the order of 100 kilocalories per gram molecule, when the ions have assumed their equilibrium distance, and so is more than sufficient to offset the expenditure of energy in the ionization process. In the vapour of NaCl and similar compounds, the molecules are thus essentially ion-pairs, but for the halides of metals with a higher ionization energy—e.g. for AgCl—the total energy change $\Delta H = I_M - E_X - U_r$ could be still endothermic, so that a molecule in which there is a covalent linkage between the atoms might be more stable.

That a pair of ions takes up an equilibrium distance apart implies that the electrostatic attraction between them is balanced by forces of repulsion which become important at short distances. Physically, we can regard the repulsion as arising when the electronic systems of the ions impinge upon each other. Since these repulsive forces vary as a high power of the distance (ranging from $1/r^5$ for helium-like ions, such as Li^+ , to $1/r^{10}$ for krypton-like and heavier ions), it is roughly true to regard the effective radius of an ion as a definite property, and the equilibrium distance between ions as given by the sum of their respective radii.

Lattice Energy.—The constitution of the isolated molecule in the vapour of a salt is far less important than the properties of salts in the solid state or in solution. In both those states factors enter into the energy balance sheet tending to stabilize the ionic bond still further—the *lattice energy* of the crystal, and the *solvation energy* of ions in a polar solvent.

As has been seen, when a pair of ions is brought together, there is a gain of electrostatic energy; in building up the regular array of ions in a crystal, such as a crystal of sodium chloride, wherein every ion is surrounded by ions of opposite sign, the nett gain of electrostatic energy is very large. Conversely, a corresponding amount of energy must be supplied to dissociate the crystals into a gas of free ions, to overcome their mutual cohesion. It is possible to compute the lattice energy of crystals (of simple structure, at least) very accurately from the laws of force between the ions, as was first shown by E. Madelung. It is greater than the energy of a single ion pair by a factor typical of each sort of crystal structure and known as the Madelung constant, which makes allowance for the number and the arrangement of ions of both signs around each ion of the crystal lattice. Thus, for the sodium chloride type of structure, the Madelung constant is 1.7476, for the zinc blende structure 1.6381. We therefore find that many compounds which,

as isolated molecules in the vapour state, would almost certainly be homopolar nevertheless form typical ionic crystals. This is, for example, typically the case for the oxides of even the more electropositive metals, such as CaO .

The general principles of electrostatics show that if a charged sphere is immersed in a medium of high dielectric constant, its potential energy is diminished by an amount depending on the dielectric constant of the medium and the radius of the cavity occupied. It is a familiar fact that the typical salts are only soluble in liquids with a high dielectric constant, such as water ($K = 80$) or liquid ammonia ($K = 22$). In such a medium the ions of both signs have their energy lowered, in accordance with the general principle, and this lowering of potential energy is equivalent to an exothermic *heat of solvation* which may be denoted S_M , S_X for the cation and anion respectively. These heats of solvation depend only upon the charge and the effective radius of the ions, not upon their nature or sign. The magnitude of the hydration energies of ions in water have, indeed, been calculated theoretically by J. D. Bernal and R. H. Fowler,² and found to agree with the experimental values.

Solvents of high dielectric constant owe that property to the fact that their molecules possess a permanent electric moment, or dipole moment (see Chap. V). In the immediate neighbourhood of an ion, the polar molecules of the solvent will tend to become oriented, though the orientation effect may not extend much beyond the shell immediately adjacent to the ion. It is in this orientation of solvent molecules that the solvation energy originates. Thus, in an aqueous solution, the water molecules around each cation will be so oriented that the negative end of the molecular dipole (that is, the oxygen atom in the bent H_2O molecule) is directed towards the cation. Each anion correspondingly attracts the positive ends of the molecular dipoles. There is no need to suppose that the ions combine with the solvent to form solvated complex ions of definite composition; the random movement of the molecules ensures that the ion is surrounded by an ever-changing atmosphere of solvent molecules, but those adjacent to the ion at any moment are oriented.

By contrast, the solvation energy of a neutral covalent molecule is likely to be but small, since the interaction between solute molecules and solvent molecules generally arises then from the interaction of dipoles in the two molecules. The hydration energies of some typical atomic ions are given in Table 3.

It will be noticed that, particularly for multivalent ions, the solvation energy adds a large exothermic term to the energy balance

² *J. Chem. Phys.*, 1933, 1, 515; *Trans. Faraday Soc.*, 1933, 29, 1049.

sheet: $\Delta H = +I_M - E_X - S_M - S_X$, and so can favour the assumption of the solvated ionic state by compounds which exist as covalent molecules in their vapour, or when dissolved in solvent of low dielectric constant. The substance will, in each case, exist in the form that corresponds to the lowest potential energy of the system.

Table 3

Heats of hydration, kilocal. per gram-ion

Li ⁺	140	Be ⁺⁺	607		
Na ⁺	115	Mg ⁺⁺	488	Al ³⁺	1150
K ⁺	94.3	Ca ⁺⁺	407	F ⁻	96.6
Rb ⁺	87.3	Sr ⁺⁺	382	Cl ⁻	64.4
Cs ⁺	80.5	Ba ⁺⁺	345	Br ⁻	57.5
				I ⁻	48.3

For this reason, the same substance in the vapour, as a crystalline solid and in solution may have its constitution determined by quite independent energetic factors. We may illustrate this by consideration of such a compound as aluminium chloride. A 'molecule' of AlCl_3 in which the binding forces were electrovalencies would be a highly endothermic entity as compared with a covalent molecule. Aluminium chloride does, in fact, vaporize forming the dimeric molecules Al_2Cl_6 (which dissociate to simple molecules at higher temperatures), and the volatility of the compound indicates that these molecules have only small external fields of force. They are, therefore, probably non-polar in character, *i.e.* are covalent molecules. They do not, however, pre-exist in the crystalline aluminium chloride from which they sublime; this has the sort of structure (co-ordination structure) typical of ionic compounds (*cf.* Chap. IV), even though the forces between the aluminium and chlorine atoms may not be purely electrostatic. We may infer that the lattice energy of the crystal is about adequate to compensate for the endothermicity of the creation of Al^{3+} and Cl^- ions. The crystal can be regarded as an infinite polymer $[\text{AlCl}_3]_\infty$, and its vaporization is essentially a chemical process, and not merely the translation of a molecule from a fixed position in the crystal into the mobile gaseous state. Dissolution is likewise an essentially chemical process (*cf.* Fig. 10). There is reason to suppose that the size of the Al^{3+} ion is such as to allow of about six water molecules being oriented around and attracted to it. Although, as has been stated, the forces operative in the hydration of the ion are probably only electrostatic, the solvation energy of the Al^{3+} ion is very great. When aluminium chloride is recrystallized from water (*e.g.* from concentrated hydrochloric acid), there is obtained not the original $[\text{AlCl}_3]_\infty$, but a hydrated crystalline compound $[\text{Al}(\text{H}_2\text{O})_6]\text{Cl}_3$ of

purely ionic structure, in which the grouping of water molecules around the aluminium persists.

Applying the considerations of the preceding paragraphs to the observed facts, as represented by the properties of the metallic

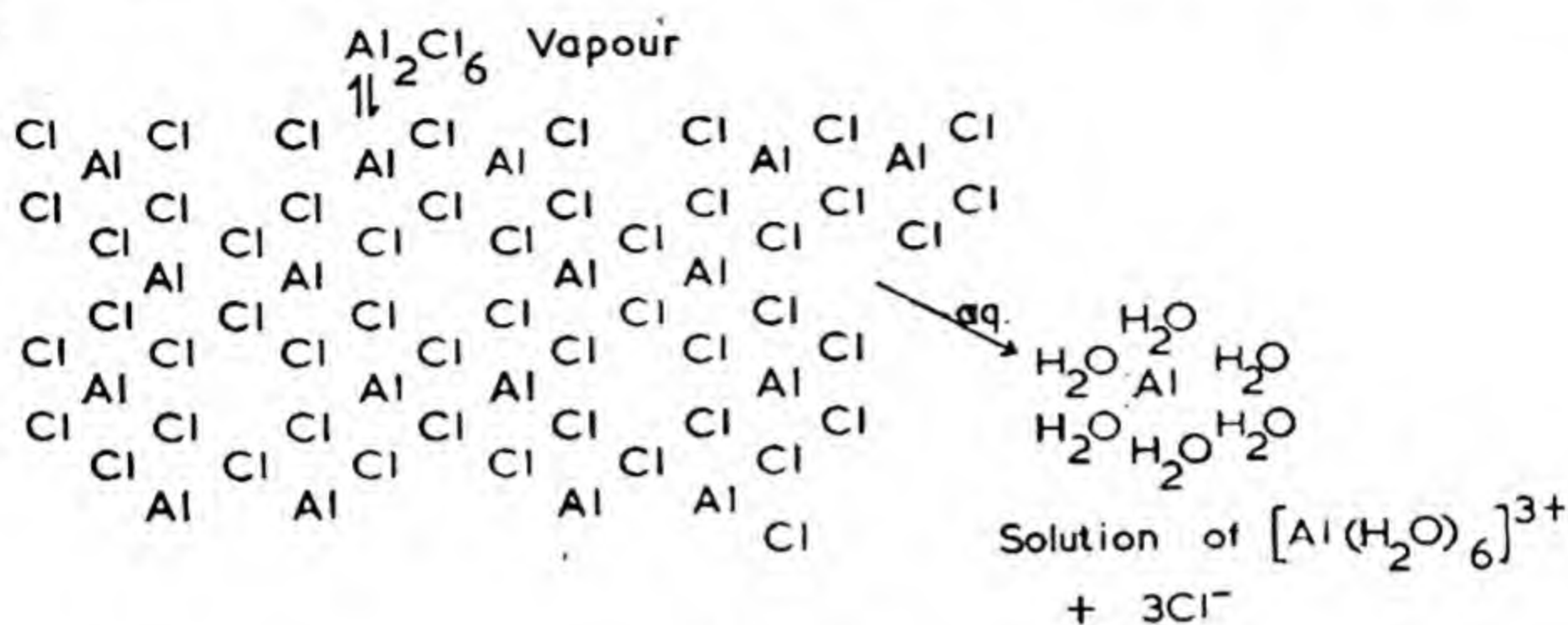


FIG. 10.

chlorides, we find a remarkably sharp demarcation between the truly ionic and the covalent chlorides, as is shown by a comparison of their fusibility, volatility, and equivalent conductivity in the molten state. The compounds fall unambiguously into one class or the other, as indicated by the dividing line in Table 4.

Table 4

	HCl	LiCl	NaCl	KCl	RbCl	CsCl
<i>m.p.</i>	− 114°	606°	800°	768°	717°	645°
<i>b.p.</i>	− 85°	1337°	1442°	1415°	1388°	1289°
<i>A</i>	10 ^{−6}	166	134	104	78	67
		BeCl ₂	MgCl ₂	CaCl ₂	SrCl ₂	BaCl ₂
<i>m.p.</i>		404°	718°	774°	870°	960°
<i>b.p.</i>		(500°)	(1000°)	(1100°)	(1250°)	(1350°)
<i>A</i>		0.066	29	52	56	65
		BCl ₃	AlCl ₃	GaCl ₃	InCl ₃	TlCl ₃
<i>m.p.</i>		− 107°	—	75.5°	586°	ca. 25°
<i>b.p.</i>		12.6°	183°	205°	(550° ?)	(100°)
<i>A</i>		0	15 × 10 ^{−6}	10 ^{−7}	14.7	10 ^{−3}

Furthermore, with elements of variable valency, the energy considerations discussed above and the high polarizing power of cations of high valency combine to make compounds derived from the highest valence states essentially covalent in character. Thus the elements of the transition series, or the B subgroups, form halides of more covalent character (Table 5), and covalent oxides or oxy-acid anions (e.g. CrO_4^{2-} , MnO_4^- , OsO_4) when exhibiting their

valency maximum, although compounds of their lower valence states may be ionic.

Table 5

	<i>B.p. of chloride</i>	<i>Conductivity of chloride at its b.p.</i>
In ^I	?	130
In ^{III}	550°	17
Tl ^I	806	46.5
Tl ^{III}	100	0
Sn ^{II}	605	21.9
Sn ^{IV}	113	0
Pb ^{II}	954	40.7
Pb ^{IV}	liq. decomp. 105°	$< 2 \times 10^{-5}$

Variability in valency amongst the metallic elements arises, in general, in two distinct ways, valid for the transition metals and for the metals of the B sub-groups of the Periodic System respectively. Whereas the valency of the metals of the A sub-groups is determined by the number of electrons external to a closed inert-gas-like core, in the centre of the long periods are successions of elements with an incomplete *d* level in the core. Thus iron, with the configuration $KL3s^23p^63d^64s^2$ in the ground state, is fairly readily ionized with the loss of the 4*s* electrons, to Fe^{++} , $KL3s^23p^63d^6$. Ionization of a further electron from the incomplete *d* level requires a much smaller expenditure of energy than does the opening up of a complete electron shell, and such a process, forming the trivalent ferric cation Fe^{3+} $KL 3s^23p^6 3d^5$, can in fact take place. Similarly in the case of copper, Cu, $KL 3s^23p^63d^{10}4s$ the single valence electron is readily ionized, forming the cuprous ion. Promotion and ionization of a second electron, leaving the Cu^{2+} ion $KL3s^23p^63d^9$, involves, however, only a few kilocalories more energy than does the ionization of the nickel atom Ni $KL3s^23p^63d^84s^2$ to the Ni^{++} ion $KL3s^23p^63d^8$, so that both cupric and cuprous compounds exist. The extension of the process to higher valencies is, in any case, limited by the energetic balance sheet, although, as has been stated, the highest valencies are exhibited only in covalent structures.

Amongst the elements of the B sub-groups, and especially amongst the elements of high atomic weight, we again find variability of valency, attributable to a somewhat different cause. In addition to the valency proper to their group, these elements form compounds—often their most stable compounds—in which they display a valency two units less.

Group :	IIIB		IVB		VB		VIB	
Valency :	3	1	4	2	5	3	6	4
	InCl ₃	InCl	SnCl ₄	SnCl ₂	Sb ₂ O ₅	SbCl ₃	TeO ₃	TeCl ₄
	TiCl ₃	TiCl	PbCl ₄	PbCl ₂	NaBiO ₃	BiCl ₃		

That these elements are more electropositive in their lower valence states accords with the preceding discussion. These elements are characterized by the presence of both *p* and *s* electrons in the outer electron shell—*e.g.* tin, with the configuration $5s^25p^2$. The spins of the *p* electrons are not coupled, and they are the more readily ionized—*e.g.* to give Sn^{++} , $5s^2$. To remove another electron necessitates uncoupling the completed $5s^2$ subgroup, so that the ionization energy is increased, over and above the amount necessary to overcome the increased electrostatic attraction of the positive ion. This effect shows itself, indeed, in the first stage ionization energies of the atoms: in the sequence Na-Mg-Al, Cu-Zn-Ga, Ag-Cd-In the ionization energy of the Group III element is, in every case, lower than that of the Group II element, which has the configuration ns^2 .

We may reasonably enquire why variability of valency is not displayed also by the elements of the A sub-groups, forming inert-gas-like cations. Their maximum valency is fixed by the stability of the inert-gas-like structure, but the possibility that such compounds as AlCl_2 or MgCl might be capable of existing in the solid state or in solution needs consideration. Numerous subhalides and analogous compounds have been reported in the past, but have in every case been disproved by later work. The heats of formation of typical compounds of this kind have been estimated by Grimm (1928), who finds that the formation of such compounds is not favoured on thermochemical grounds, and that for many a disproportionation process—*e.g.* $3\text{AlCl} \rightarrow 2\text{Al} + \text{AlCl}_3$ —would be exothermic. This conclusion follows largely because the first stage ionization energies of the Group II and III metals is far higher than that of the alkali metals.

In solution, similar considerations arise from the interplay of ionization energies and hydration energies. There is no reason why compounds incapable of existing in the solid state should not be formed in solution; studies of reactions at the dropping mercury cathode, whereby the transient formation of reduced ions can be detected, have indeed revealed instances of the step-wise discharge of multivalent cations. This is the case, for example, with the rare earths at a mercury cathode. Such cations are, however, likely on thermochemical grounds to discharge hydrogen ions from the solvent, liberating hydrogen and forming the cations of normal valency. In such a case, the compounds of the lower valence state

will be unstable in aqueous solution and will be formed only under conditions of high hydrogen overvoltage such as obtains at a mercury cathode, or in reduction by base metal amalgams.

Whilst sub-compounds are likely to be unstable in solution, or as ionic crystals, they may nevertheless exist as isolated covalent molecules in the vapour state. Such species as AlCl , which have been identified spectroscopically, can be formed freely by the action of the more stable halide upon the metal, but undergo disproportionation when they are condensed. Reactions of the type $\text{AlCl}_3(g) + 2\text{Al}(s) \rightleftharpoons 3\text{AlCl}(g)$ may then be reversible. It is clear that the limitations that govern the accessible valence states of the metals in *ionic* compounds cannot necessarily be applied to compounds in which the bonding is covalent.

Covalency.—The precise treatment of the covalent bond is a much more difficult problem than is the treatment of electrovalency. There have been three main approaches to the subject, each laying stress on some one aspect of the covalent bond. The Heitler-London method treats the problem essentially by considering the mutual neutralization of electronic spin by two atoms; Pauling and Slater, from a consideration of the wave functions of the electrons in the isolated atoms, have shown how the quantum theory leads to the conception of directed valency; Hund and Mulliken relate the energy of these electrons to parameters of the molecule as a whole in the method of molecular orbitals. The rigorous quantitative application of any of these methods is restricted, by mathematical difficulties, to the simplest cases. Even a qualitative consideration of their essential features serves, however, to give a deeper insight into the mechanism of chemical binding than is obtainable from the very approximate and excessively qualitative, but yet suggestive, Lewis-Langmuir treatment.

Heitler and London first successfully calculated the potential energy of a system of two hydrogen atoms as these were brought closer together. The essential result of this calculation may be summarized as follows. The electrostatic, or Coulomb, forces between two nuclei and two electrons give rise to a nett weak attractive force only. There is, however, a second type of interaction which arises from the properties peculiar to the wave mechanical electron: namely, that an electron is not confined to a localized orbit, but has a certain probability of being found elsewhere in space (see p. 15). If we have two hydrogen nuclei A and B, electron 1 being associated with nucleus A, electron 2 being associated with nucleus B, such a state is indistinguishable from that which results from interchanging the electrons so that electron 2 is associated with nucleus A, electron 1 with nucleus B.

This amounts to saying that each electron has an equal probability of being found on either atom, and that each nucleus can be associated with both electrons. The amplitude Ψ^2 of the wave function of each electron does, however, fall off very rapidly with the distance from the nucleus. For this reason, except when the distance between the nuclei is of atomic dimensions, the probability or frequency of exchange of electrons between the atoms is negligibly small. If the atoms are brought close together, the operation of Pauli's exclusion principle makes the energy of the system dependent on the spin quantum numbers of the electrons. If the spins are parallel, both electrons can only find orbits around one nucleus if one electron is excited to a higher—*e.g.* the $2s$ -quantum state. The potential energy of the system is then *higher* than that of the isolated atoms, and their approach brings repulsive forces into play. If the electron spins are opposed, so that the resultant spin is zero, both electrons can be accommodated in orbits of the lowest energy about either nucleus. The energy of the system is then *lower* than that of the isolated atoms: attractive forces are operative and a stable molecule results. The so-called *exchange energy* arising in this way accounts for about 80 per cent of the observed energy of formation of the hydrogen molecule. For the case of parallel electron spins, the model implies that the wave functions of the electrons have opposite phase between the nuclei; the amplitude is therefore less between the atoms than around an isolated atom, and the electron density falls to zero between the atoms, being accumulated rather on the remote side. With opposed spins the wave functions reinforce one another, and the electron density has a maximum at the mid-point. We can, indeed, regard the binding force as arising from the electrostatic attraction of the nuclei for this accumulated electron cloud between them. This model thus reveals the significance of the electron pair bond of the Lewis-Langmuir theory; it leads to the conclusion that only those atoms with unpaired electrons can form covalent bonds, and it equates the valency of an atom directly to the number of unpaired spins.

Pauling and Slater, accepting the essential results of the Heitler-London theory, have shown that in conjunction with a consideration of the spatial distribution of electron density it is possible to devise a formal theory of directed valence forces consistent with the ideas current in chemistry since the days of van't Hoff and Le Bel. The existence of a high electron density between two linked atoms means that their wave functions overlap in that region of space: the electrons have a high probability of being found on either atom. Pauling considers as a general principle, that the greater the overlap of wave functions, the stronger the bond formed. It is

in this respect that the properties of p wave functions take on a special importance, for, as has been seen in Chapter I, the maximum electron density lies along the axis of the wave function, and since the electron can be thought of as spending most of its time near this axial direction, the electron density is greater along this axis than at any point in a spherically symmetrical s wave function of similar total energy. Stronger bonds are formed with p electrons than with s electrons, accordingly, and the requisite maximum overlap of wave functions is attained when the bound atoms lie along the axes of the wave functions.

The distribution of electrons in an incompletely filled p or d subgroup is governed by an empirical rule known as the rule of maximum multiplicity, which states that the energy of interaction between the electrons in any one atom is a minimum when their resultant spin is greatest. This means that as electrons are added

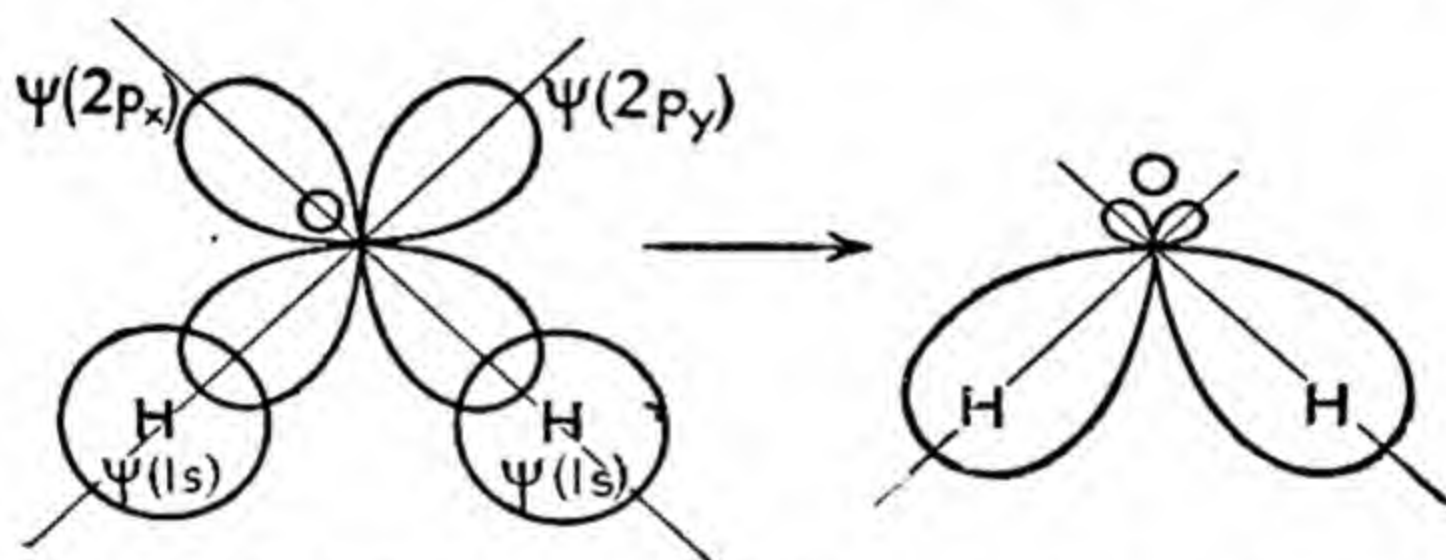


FIG. 11.—Diagrammatic representation of interaction between hydrogen and the p electrons of oxygen in H_2O .

successively, as many orbits as possible are singly occupied before any pairing of electronic spins is permitted. In the oxygen atom, therefore, with four $2p$ electrons, all three p orbits are tenanted: one orbit—*e.g.* the p_x orbit—is full, with two electrons, the p_y and p_z orbits being singly occupied. The atom is, therefore, divalent, having two unneutralized spins which may be coupled with the electrons of two hydrogen atoms. The requisite condition of maximum overlap of wave functions is attained when hydrogen atoms are brought up along the y and z axes, respectively (Fig. 11). Hence, to a first approximation, in the molecule of water, the two O—H valencies should be directed at right angles. In the same way, the molecule of ammonia should be pyramidal with hydrogen atoms located along the x , y , and z directions. The 90° valence angle derived from this very approximate picture does not take account of repulsions between the hydrogen atoms and other perturbing factors, and in fact, the valence angles in simple molecules such as H_2O , NH_3 are greater than 90 degrees.

Hybrid Orbitals.—The quadrivalency of carbon presents an interesting problem in the Pauling-Slater treatment. In its ground state, the carbon atom has the configuration $1s^2 2s^2 2p^2$, with two spins unpaired in accordance with the maximum multiplicity rule, and it might be expected to be divalent. To exert four valencies it is necessary to excite one of the $2s$ electrons to the third $2p$ state giving the configuration $1s^2 2s 2p^3$, with four unpaired spins. It would appear at first sight that from this configuration there would be formed three strong bonds, directed roughly orthogonally, as in ammonia, and one weaker bond, located in whatever direction was sterically convenient. In fact, the equivalence of the four valencies of carbon is most firmly established. Pauling introduced into valency theory in 1931 the conception that, in some instances, the strongest bonds may be formed not from pure s or pure p wave functions, but from certain combinations of these, known as *hybrid orbitals*. A mechanical vibrating system, such as a vibrating disc, will possess a number of independent normal vibrational modes, and may, moreover, vibrate simultaneously in more than one mode. The resulting composite vibrations may be described as superpositions of two or more of the independent modes of vibration of similar energy. In similar manner, since the wave functions describe, essentially, the distribution of electron density it is permissible—subject to certain restrictions which cannot be discussed at this place—to introduce a new set of wave functions which leads to the same total electron density distribution. From the combination $2s 2p^3$ of the quadrivalent carbon atom, the s and p states can be so combined that four new mutually equivalent wave functions are obtained, directed towards the apices of a regular tetrahedron; the bonding power of these wave functions, which may be denoted $[sp^3]$ orbitals, is stronger than that of a pure p wave function, or of any other hybrid function that can be obtained from s - p orbitals. The equivalence of the carbon valencies, and their steric arrangement, are thus related directly to the condition that the strongest possible bonds should be formed.

This sort of 'hybridization' is believed to play an important role in the formation of covalencies by atoms of other elements than carbon. Amongst the lighter elements, the boron atom forms three equivalent bonds; as the ground state has the configuration $2s^2 2p$, trivalency implies that one electron must first be promoted, giving the configuration $2s 2p^2$. The strongest bonds in such a system would be formed from three coplanar $[sp^2]$ orbitals, oriented at 120 degrees to one another in accordance with the known stereochemistry of boron (*cf.* Fig. 12). In a similar manner, the elements of Group II have an s^2 ground state, but in their covalent com-

pounds such as $\text{Zn}(\text{CH}_3)_2$ or HgBr_2 the bonding orbitals are $[sp]$ hybrids and the resulting bonds are collinear: the bound atoms lie all in the same straight line, in contrast with the valency angle of 90–105 degrees associated with bonding by the orbitals of the Group VI elements. The valence properties of the heavier elements are determined by just the same considerations as those of the elements of the first short series of the Periodic Table, as long as only s and p orbits come into play. In the transition series, however, the partly unfilled d orbits are similar in energy to the s and p orbits of the outermost quantum shell. Hybrid orbitals formed by the combination of d and s , or d , s , and p orbitals have particu-

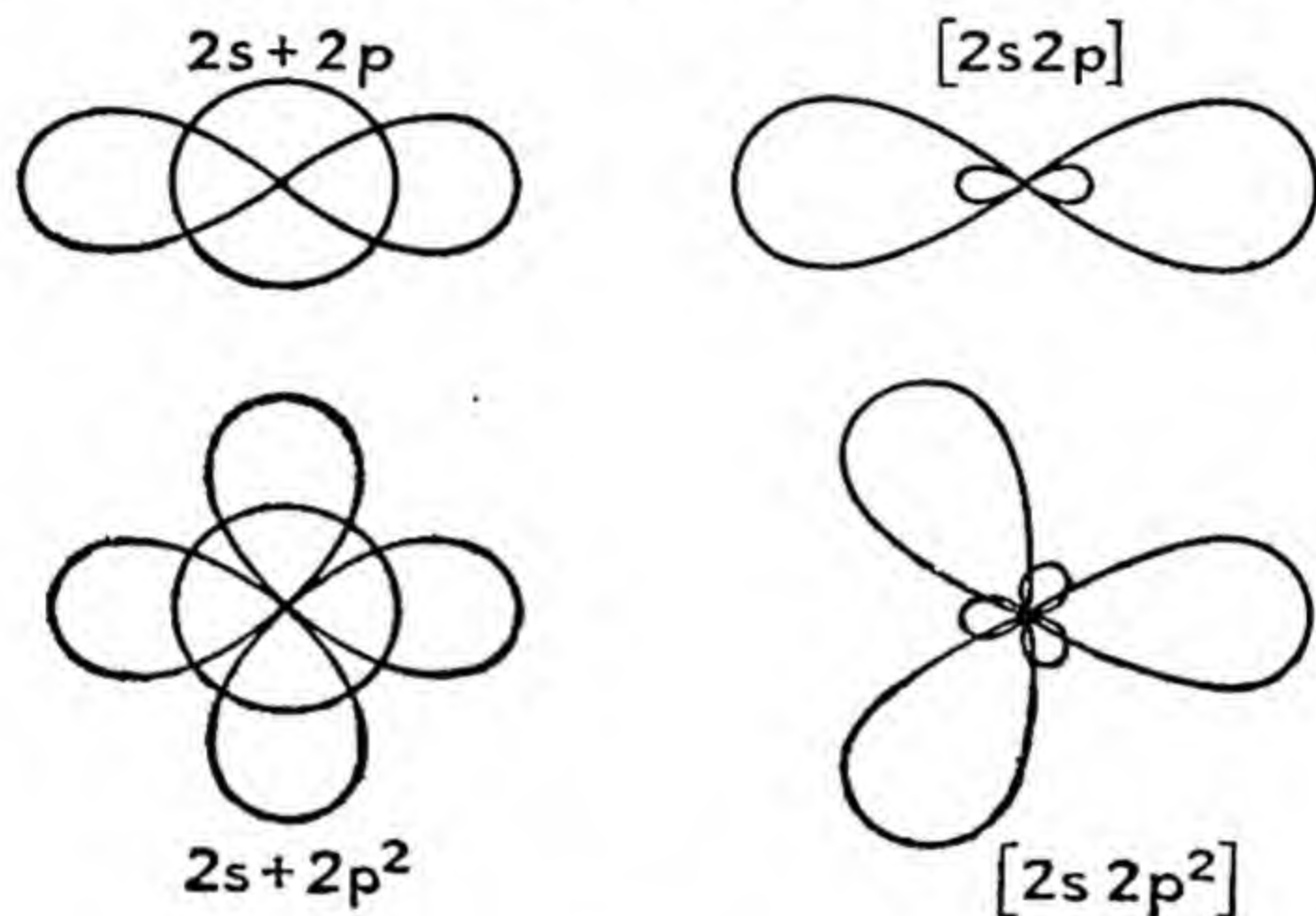


FIG. 12.

larly strong bonding power, and as will be seen in Chapter VI, the formation of covalent bonds by such hybrid orbitals dominates the chemistry of the elements at the end of the transition series. It may be noted here that by hybridizing two d , one s and three p wave functions, six strong bonds disposed towards the vertices of an octahedron are obtainable, and from one d , one s , and two p wave functions, four equal and coplanar strong bonds. These two types of hybrid orbitals give rise to two stereochemical classes which determine the properties and the stereochemistry of many metallic compounds, and which are second in importance only to the tetrahedral bond class found in carbon.

Every approach to the theory of valency is essentially approximate; those considered hitherto neglect the fact that the normal quantization of the electrons must be broken down when two atoms approach to the closeness implied by chemical bonding. As a result,

the principal and subordinate quantum number n and l have little meaning; only the quantum numbers signifying the component λ of orbital angular momentum along the line joining the atomic centres are significant. Corresponding to the designation s , p , d , etc., for values $l = 0$, 1 or 2, in the isolated atom, electrons for which λ is 0 ± 1 or ± 2 are termed σ , π or δ electrons, respectively. In the method of molecular orbitals, the wave function of the molecule is built up by feeding electrons successively into the molecular framework, beginning with the orbitals of lowest energy. Each electron is then treated as belonging to the molecule as a whole, and its nature as a σ , π , δ , etc., electron may be found unambiguously; the relative order of the molecular orbitals so filled is non-committally denoted by alphabetical symbols. In Mulliken's convention, orbitals in the order of increasing energy are represented by $z < y < x < w$, etc.

As electrons are fed successively into the molecular orbitals, series of closed groups are built up in a way analogous to the manner in which closed shells arise in building the extra-nuclear structure of an isolated atom. An s electron (in an isolated atom), having zero orbital angular momentum l , must also have zero orbital angular momentum along the internuclear line when fed into a molecular orbital. λ is then zero, and an s electron accordingly becomes a σ electron. A p electron, however, with $l = 1$, may have $\lambda = +1$, 0 or -1 , depending on the component of l along the line of centres; it may therefore become either a σ or a π electron in the molecular orbital. For each value of λ , there are two permissible values for the spin quantum number ($\pm 1/2$), in accordance with the Pauli principle. Two electrons may then be inserted in each σ orbital, and four electrons in each π orbital. We may summarize the process in the following table:

Table 7

Complete electron shells in isolated atom	l	Possible values of λ	Complete electron groups in molecule
s^2	0	0	σ^2
p^6	1	$0, \pm 1$	σ^2, π^4
d^{10}	2	$0, \pm 1, \pm 2$	$\sigma^2, \pi^4, \delta^4$

Each group of two σ , four π , and four δ electrons thus constitutes a closed shell; as each such shell is filled, the next electron to be added must be placed in the next higher orbital.

The placing of the orbitals in their correct energetic order for any pair of atoms follows from the application of certain rules worked out by Hund and Mulliken. For a full consideration of these rules the reader is referred to more detailed works upon the subject;³ the ingenious principle upon which the succession of orbitals is based is readily made clear, however, by means of a simple example, and is illustrated diagrammatically in Fig. 13. Mulliken supposes two

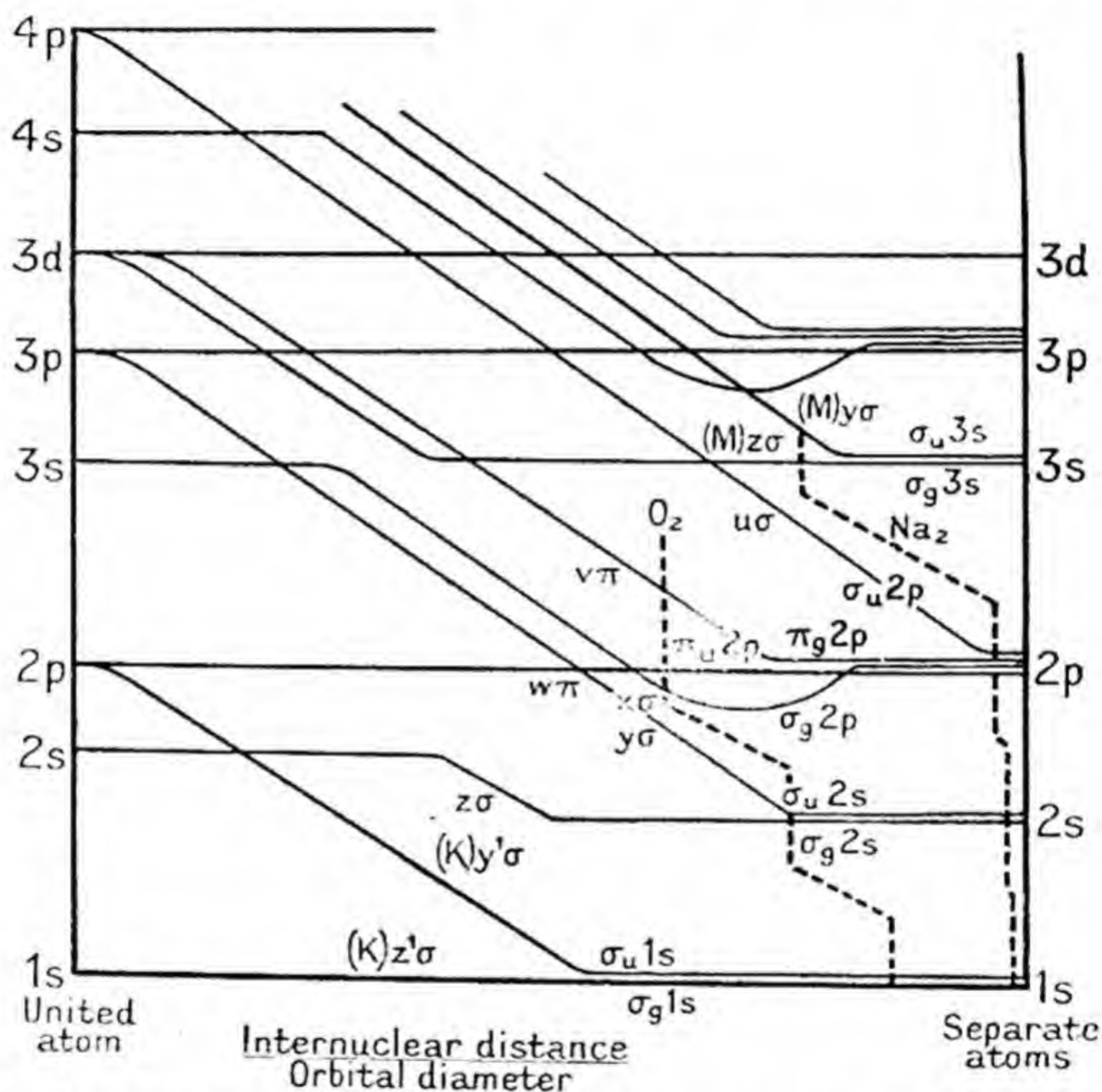


FIG. 13.—Mulliken correlation diagram for like atoms. The dotted lines indicate the filling of orbitals in O_2 and Na_2 , respectively.

isolated atoms to be brought up to one another until, when the internuclear distance is zero, the nuclei coalesce, forming a new compound atom. The electronic configuration of the isolated atoms is known, as also is the configuration of the compound atom, since this is simply an atom with atomic number equal to the sum of the nuclear charges of the two separate atoms. What happens to the electrons in passing from the isolated atoms to the compound

³ Cf. Kronig, *Optical Basis of the Theory of Valency*, Cambridge, 1935, pp. 124, 201; an excellent review is given by van Vleck and Sherman, *Reviews of Modern Physics*, 1935, 7, 168.

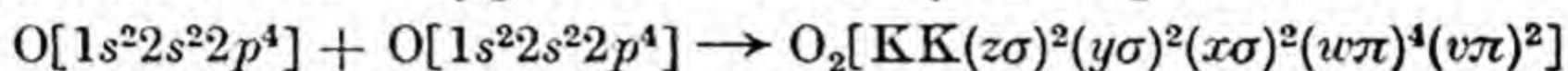
atom may be deduced from considerations of symmetry alone. Let us consider the case of two hydrogen atoms. Each, in the isolated state, has one $1s$ electron. The coalescence of the nuclei produces a nucleus of charge 2—*i.e.* a helium nucleus. The first $1s$ hydrogen electron to be added goes at once into the $1s$ level of the compound atom. If the second electron has an antiparallel spin, it also goes into the $1s$ level of the compound atom, completing the $1s^2$ pair. This would constitute a stable configuration, showing that the interaction between two adjacent hydrogen atoms when the electrons have opposed spins would be bonding. If, however, the spin of the second electron was parallel to that of the first, it could not enter the $1s$ level of the compound atom without infringing the Pauli principle. Considerations of symmetry show, in fact, that it must enter the $2p$ state of the compound atom, which then receives the configuration $1s2p$. This represents a highly excited state of a helium atom, and would require the absorption of a large amount of energy. Hence it must correspond with a repulsive interaction between the hydrogen atoms, due to the parallel spins of the electrons. In general, any electron which has to be promoted to a level of higher principal quantum number in passing from the isolated atoms to the compound atom is antibonding in action. Complete closed shells (*i.e.* K and L shells) are practically unaffected by the proximity of a second atom, and so are treated as non-bonding. Mulliken has published tables of correlation between the initial and hypothetical final states from which the relative energetic positions of the orbitals may be deduced in that intermediate stage which corresponds with actual chemical combination.

The qualitative application of the method may be shown by considering a few examples. The molecule F_2 must be formed by the union of two atoms having the configuration $1s^2 2s^2 2p^5$. On comparison with Mulliken's correlation data, the orbitals occupied in F_2 are $[KK(z\sigma)^2(y\sigma)^2(x\sigma)^2(w\pi)^4(v\pi)^4]$. The K shell remains unaffected; there are four electrons, originally in the $2s$ state, which are accommodated in the $z\sigma$ and $y\sigma$ orbitals; there remain 10 $2p$ electrons which are inserted successively into the $x\sigma$, $w\pi$ and $v\pi$ orbitals (Fig. 13). It may be seen that the $(z\sigma)^2$ and $(y\sigma)^2$ electrons are bonding and antibonding, respectively; of the remainder, the $x\sigma$ and $w\pi$ electrons are not promoted, and thus are bonding, whereas the $v\pi$ are promoted and are therefore antibonding. There are thus eight bonding and six antibonding electrons in all, *i.e.* a nett bonding effect of two electrons, constituting a single bond, but the interaction of all the electrons outside the K shells is considered.

In the same way, the formation of N_2 may be formulated as $N[1s^2 2s^2 2p^3] + N[1s^2 2s^2 2p^3] \rightarrow N_2[KK(z\sigma)^2(y\sigma)^2(x\sigma)^2(w\pi)^4]$. Here,

as before, $(z\sigma)^2$, $(x\sigma)^2$ and $(w\pi)^4$ are all bonding; $(y\sigma)^2$ is antibonding. Hence there is a resultant effect of six bonding electrons, corresponding to a triple bond.

The power of the method is shown by its application to the oxygen molecule. Oxygen, diatomic sulphur (S_2) and sulphur monoxide are all paramagnetic. This is to be associated, as will be discussed in a later chapter, with the presence of unpaired electronic spins. The magnetic moment of oxygen corresponds to the existence of two unpaired electrons in the molecule. Such a conclusion is at variance with the other approaches to the subject of valency, since the formation of a double bond might be expected. It follows directly from the molecular orbital method, however, since the formation of the oxygen molecule may be represented



It has been seen that four π electrons—as, for example, the $(w\pi)^4$ group—constitute a closed group; hence the $v\pi$ orbital, occupied by only two electrons, is only half-filled. The electrons can therefore set themselves with their spins either coupled to zero or parallel. In accordance with the maximum multiplicity principle, the state of lowest potential energy will be that in which the electronic spins are parallel, so that the ground state of the molecule is paramagnetic.

A correlation diagram analogous to Fig. 13 may be drawn up for the interaction of unlike atoms also, and by its use the electronic configuration of diatomic molecules may be worked out. It is found that isosteric molecules have identical electronic configurations. Thus, the orbitals occupied in carbon monoxide are those which are also involved in the nitrogen molecule:



The important result emerges that carbon monoxide has, as many lines of evidence demand, a triple-bonded structure. The triple bond has no 'semipolar' character, however, so that the absence of a dipole moment, which would be expected to be high from the formulation $C \equiv O$, is at once comprehensible.

For diatomic molecules, the energies of the molecular orbitals may be correlated directly with spectroscopic data, and the molecular orbital model may be precisely defined. Any rigorous extension of the method to polyatomic molecules is, however, practically impossible, and it is therefore necessary to make the approximation that the molecular orbitals of the polyatomic molecule can be built up from those of each pair of bonded atoms, considered by itself, a method termed by Mulliken the linear combination of atomic orbitals. This amounts to the assumption that the overlap

of wave functions in any one bond does not modify the electron density distribution between other bonded pairs of atoms. Such an approximation is only partially true, and many of the finer aspects of chemical reactivity, especially as illustrated in the behaviour of organic compounds, turn on just such second-order effects.

Mesomerism or Resonance.—No single approach to the quantum theory of valency gives a completely accurate representation of the facts. Thus, the Heitler-London and Pauling-Slater methods explicitly ignore 'ionic' terms, *i.e.* the probability of finding both electrons of a covalency simultaneously upon one or other atom. Calculations based on the method of molecular orbitals, in attempting to give the time average of electron density over the molecule, overweight just these ionic terms. Since, however, the complexity of the problem prohibits the strict calculation of bonding energies, save for the simplest types of diatomic molecules, the value of the theories lies chiefly in the formal representation they afford of the bonding process, and the chemist is therefore entitled to utilize whichever is most adapted for his purposes. The very approximate Lewis-Langmuir-Sidgwick approach to the electronic theory is thereby amply justified.

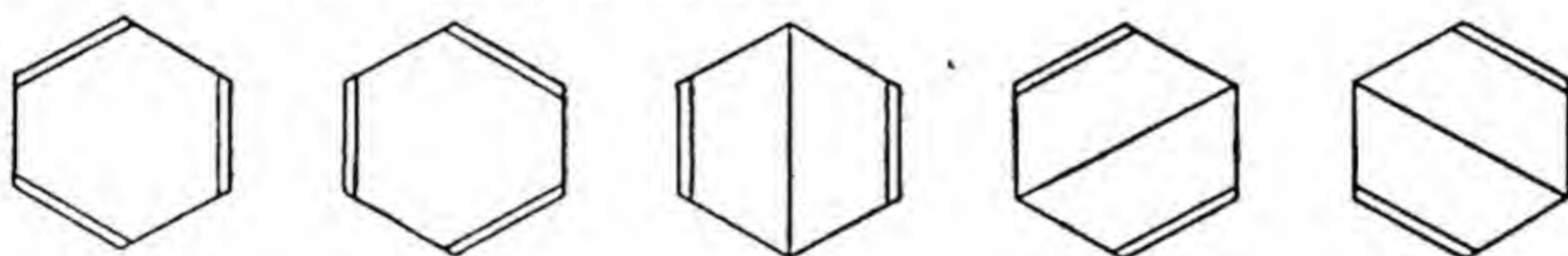
Conversely, it is true in many cases that no single chemical formula is an adequate representation of the bonding in a given molecule. The division into ionic bonds, single, double and triple covalent bonds represents rather the definition of limiting types than a universally valid classification. Thus, in a covalently linked pair of atoms $A-B$, the probability of finding both the valency electrons on A may be greater than that of finding them on B . The molecule AB will then have a resultant dipole moment,

$(\delta-) (\delta+)$
 $A-B$; the resulting electron density distribution may be regarded as produced by superposing the configurations $A-B$ and $A^- B^+$ in suitable proportions. The resulting bond is thus intermediate between an ionic valency and a pure covalency, and possesses a finite dipole moment. In the same way, a covalency may be intermediate in order between a single and a double bond.

This conception is particularly important when the formula of the molecule, as written conventionally in two or more different ways, leads to nearly the same value for the potential energy, while preserving the same spatial arrangement of the atoms. Not only is the resultant distribution of electron density the weighted mean of those corresponding to the various formulæ (as follows from the preceding paragraph), but it emerges from the quantum theory that the potential energy of the system is, in such a case, considerably lower than that for any of the component states. This idea is already inherent in the Heitler-London treatment of covalency,

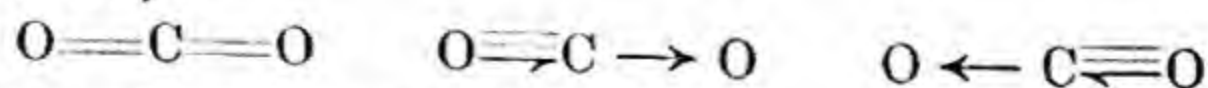
which hinges upon the indistinguishability of configurations in which electrons are interchanged. The exchange energy which provides the major contribution to covalent binding is essentially a resonance energy. This phenomenon is termed *resonance* or *mesomerism*, and the resulting state of the molecule is frequently termed a *resonance hybrid* of the component states. The latter term is misleading. There is no oscillation or tautomerism between the various formulæ; the electron density is rather evened out so as to correspond with an intermediate state. In addition to lowering the potential energy (*i.e.* increasing the stability) of a molecule, mesomerism results in the shortening of interatomic distances in the bonds concerned. Much of the evidence for mesomerism is, in fact, based upon the measurement of bond lengths by the methods referred to in Chapter V.

The most obvious case of resonance is that of aromatic nuclei. For benzene there may be written the two Kekulé structures, exactly equivalent energetically, and three equivalent Dewar structures at a slightly higher energetic level:



The actual state is therefore a hybrid, intermediate between all these possible forms, so that the ring is actually formed, not of alternating single and double bonds, but of six equivalent bonds of the order 1.5. Alternatively, we can consider the regular hexagon frame work to be bound by bonds between $[sp^2]$ type hybrid wave functions, leaving one p electron on each carbon atom not yet utilized. These p electrons combine to form one half-filled molecular orbital, a standing electron wave extending over the whole aromatic ring. It will be apparent later (Chap. XV) that such an extended molecular orbital, in aromatic compounds or other conjugated systems, bears distinct analogies to the electrons of a metal, moving freely over long paths in a periodic atomic field.

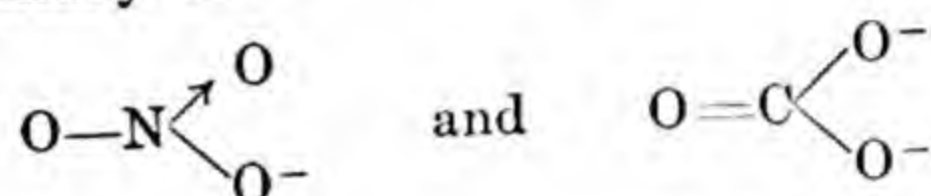
The application of the conception of resonance to many problems of organic chemistry is obvious. It is of more immediate interest that the phenomenon is met with also in some simple inorganic molecules.⁴ Thus the formula of carbon dioxide could be written in the three ways



⁴ See Sidgwick, *J.C.S.*, 1936, 533; 1937, 694; *Ann. Rep. Chem. Soc.*, 1934, 31, 38.

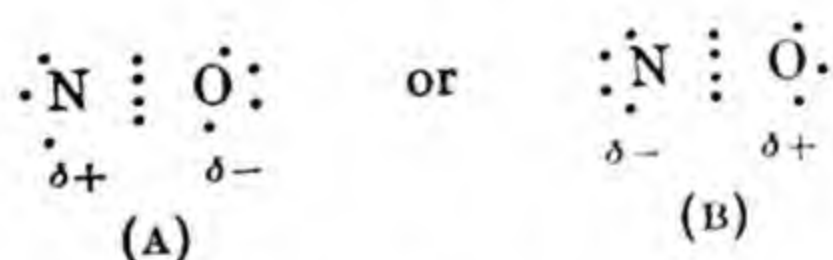
For each of these the heat of formation (from atomic carbon and atomic oxygen) should be about 350 kilocal., and the O—O distance should be 2.56 Å in each case. The observed heat of formation and oxygen-oxygen distance are 380 kilocal. and 2.30 Å, respectively, indicating that the resultant state is a hybrid of the three possible formulæ. Since, moreover, the second and third formulæ are equivalent, they must be represented to equivalent extents in the hybrid, which is thus non-polar.

In the same way, the oxygen atoms in the carbonate and nitrate ions, written formally as



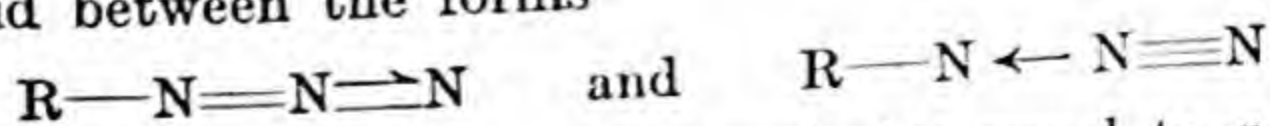
become equivalent by a resonance process, any distinction between single, double or co-ordinate links vanishing. The equilateral triangular configuration of the CO_3^{2-} and NO_3^- ions, established by X-ray crystallography, is thereby justified.

Where the limiting forms have large, but opposed, dipole moments, the effect of resonance must be to lower or even annul the dipole moment of the whole molecule. Thus nitric oxide may be written either as



In the resulting resonance hybrid, the two forms are represented to slightly different extents, giving a resultant dipole moment of 0.16×10^{-18} e.s.u.—very much less than that of either structure separately. It should be noted that the profound difference between resonance and tautomerism is well exemplified here: a tautomeric mixture of the two structures (A) and (B) would have a high moment—equal, in fact, to the weighted mean of the moments of the separate structures. It is also important to observe that the description of the actual state as a hybrid of (A) and (B) amounts to the same thing as the formulation of NO by the method of molecular orbitals— $\text{NO}[\text{KK}(z\sigma)^2(y\sigma)^2(x\sigma)^2(w\pi)^4(v\pi)]$, in which the odd electron is not assigned to either atom, but to an orbital of the whole molecule.

A similar resonance state is presented by the azide radical, which is a hybrid between the forms



with a resultant dipole moment practically equal to zero.

There is some evidence also of resonance in the non-metallic

halides. Thus, whereas the C—Cl distance observed in CCl_4 agrees with that calculated from independent measurements of the atomic radii, a very appreciable contraction is found in the tetrachlorides of silicon, tin and germanium.⁵ The difference is attributed to the completion of the second quantum level in the carbon compound, so that no more than four bonds can be formed. Hence, carbon-chlorine links of the type $\text{C}\equiv\text{Cl}$ in carbon tetrachloride are excluded. In the tetrachlorides of the higher elements of Group IV, the formation of more than four bonds is possible, so that the resonance form $\text{Cl}_3\text{X}\equiv\text{Cl}$ can make an appreciable contribution to the configuration of the whole.

⁵ Brockway, *J. Amer. Chem. Soc.*, 1935, 57, 958. Sutton, Hampson *et al.*, *Trans. Faraday Soc.*, 1937, 33, 852: see also Wells, *J.C.S.*, 1949, 55.

CHAPTER IV

THE CONSTITUTION OF SOLID INORGANIC COMPOUNDS

In the development of chemical theory, the state of matter which has been most fully studied, and which has yielded the most information, is the molecular-disperse state, as found in gaseous substances and in solutions. The solid state of matter is particularly important, however, in the domain of inorganic chemistry. Many inorganic compounds exist only in the solid state; a crystalline salt is not identical in nature, stability and properties with the solvated ions that it furnishes when it is dissolved in a polar solvent. The manner in which the graduated chemical properties of the elements manifest themselves in the physical and chemical properties of their compounds, and the mechanism of reaction processes in solids, all receive considerable illumination from the knowledge that has been amassed in recent years about the solid state. The principles of this field of chemical study find their exemplification throughout the descriptive chemistry of the elements, and references to the crystal structure of the elements and their compounds will repeatedly be made in the subsequent chapters of this book.¹

The characteristic external symmetry and optical properties of crystals are strongly suggestive of some regularity of internal structure, and as early as 1784 Haüy suggested that crystals could be conceived as built up by stacking together minute regular structural units, each with the symmetry of the whole. Haüy's early speculations gave place, through the work of Bravais (1848), Sohncke (1879), Federov, Barlow and Schoenflies (all between 1890-94), to the rigorous geometrical investigation of the properties of space lattices—i.e. three-dimensional arrays of points, making up a regular repeating pattern. By 1912, when von Laue, Friedrich and Knipping demonstrated the diffraction of X-rays by crystals,

¹ For more detailed discussion of the subject matter of this chapter, the reader is referred especially to A. F. Wells, *Structural Inorganic Chemistry*, Clarendon Press, 1946; R. C. Evans, *Crystal Chemistry*, Cambridge University Press, 1939; W. L. Bragg, *Atomic Structure of Minerals*, Oxford University Press, 1937; and C. W. Bunn, *Chemical Crystallography*, Oxford University Press, 1946.

the purely geometrical theory of crystallography had probably progressed as far as was possible.

In real crystals, the points of the lattice theory represent the mean positions of atoms—mean positions, because the atoms execute thermal vibrations about them at all temperatures above the absolute zero. All points of any one space lattice must be occupied by like atoms, so that in a compound we may consider the atoms to lie on two or more interpenetrating space lattices. For example, in sodium chloride the sodium atoms and chlorine atoms each lie on the points of a face-centred cubic space lattice, the two space lattices being displaced by a distance $\frac{1}{2}a$ along each of the three axial directions.

In a crystal lattice built up in this way we may recognize a *unit cell*, or unit of pattern, containing as many atoms of each kind as are required to conform to certain symmetry requirements (determined by the 'space group' of the crystal). It is the task of X-ray crystallography to determine the dimensions of this unit and the position of every atom within it. The empirical formula of a compound is generally contained once, or some integral number of times, within the unit cell. This is, however, not quite invariably the case, for in high molecular compounds (e.g. cellulose, fibrous proteins, stretched rubber and $[\text{PNCI}_2]_n$) the molecule itself is built up by the manifold repetition of a certain unit of pattern which, by the association of a group of adjacent, oriented chains, constitutes also the unit of the crystal lattice.

The Determination of Crystal Structure.—The possibility of transcending the limitations of formal crystallography arose in 1912, when Friedrich and Knipping, in course of testing von Laue's hypothesis that the wave-length of X-rays should be comparable with the inter-atomic distances in a crystal, observed that a pencil of X-rays formed a diffraction pattern on a photographic plate when it was passed through a crystal of zinc blende.

In such an experiment, the atoms in a crystal act as scattering centres for the incident X-ray beam, and since they can be roughly assigned to definite positions in a three-dimensional network, they constitute, in effect, a three-dimensional diffraction grating. The regular array of atoms in the space lattice implies that one can distinguish certain sets of parallel and equally spaced planes in the crystal, containing a high density of atoms. When a beam of X-rays passes through the crystal, the X-rays diffracted by atoms in successive planes of such a set will mutually extinguish each other unless the contributions of adjacent planes are in phase. If the distance between successive planes is d , and the grazing angle of incidence is θ , the path difference between X-rays scattered from

neighbouring planes is $2d \sin \theta$. The condition that X-rays of wave-length λ shall be reflected by any family of planes is then given by the Bragg relationship

$$n\lambda = 2d \sin \theta$$

The distance d is directly related to the dimensions of the unit cell and the Miller indices of the reflecting planes.

The Bragg law is fundamental to the study of crystal structure. The data needed in order that a crystal structure may be worked out involves, in principle, measurements of two quantities, (a) the angle of diffraction and (b) the intensity of each diffracted beam.

(a) If we employ X-rays of known wave-length λ we obtain from the angle of diffraction θ the inter-planar spacing d corresponding to each 'reflection'. The most important of these inter-planar spacings will be the parameters, defining the unit cell of the structure. When these fundamental dimensions have been measured, it is possible to deduce the identity (*i.e.* the Miller indices) of every family of planes that gives rise to a reflection.

(b) Every atom in the lattice acts as a scattering centre for X-rays, so that the total intensity of the diffracted beam in any direction depends on how far the contributions of the individual atoms are in phase. That is, the intensity of the diffracted beam depends on the arrangement of atoms within the unit cell. For any given arrangement of atoms within the cell, it is possible to calculate theoretically the diffracting power of every family of planes (*i.e.* the ratio of *intensity of diffracted beam* to *intensity of incident beam*). The essence of crystal structure determinations is the trial-and-error search for that arrangement of atoms which would best account for the observed intensity of reflection from all families of planes.

Experimental Methods.—Several distinct experimental methods are available for obtaining the data referred to in the previous paragraph. For a proper discussion of the technique of crystal analysis, reference must be made to books on that subject,² but we may sum up the principles of the most important methods as follows, classifying them according as they use (a) 'white' or monochromatic X-rays; (b) stationary or moving crystal specimens; and (c) single crystal or polycrystalline specimens.

(i) Laue method. This employs 'white' X-radiation—*i.e.* X-rays having a range of wave-lengths, usually excited by bombarding a tungsten target with cathode rays having energy (usually 50–60 kilovolts) insufficient for the excitation of the K-radiation of tungsten.

² See W. H. and W. L. Bragg, *The Crystalline State*, Vol. I, Bell, 1949; C. W. Bunn, *Chemical Crystallography*, Clarendon Press, 1946; N. F. M. Henry, H. Lipson and W. A. Wooster, *The Interpretation of X-ray Diffraction Photographs*, MacMillan and Co., 1951.

If a pencil of such X-radiation is passed through a stationary crystal, a diffraction pattern, related to the symmetry of the crystal about the axis of transmission of the X-ray beam, may be recorded on a photographic plate. Each spot corresponds with the satisfaction of the Bragg relation by some particular family of planes, the spacing d , the inclination θ to the X-ray beam and the wavelength λ all being variables. Intensity relationships in Laue photographs are difficult to assess; the method is therefore used chiefly for the assignment of space groups, rather than for complete structure analysis.

(ii) Bragg method. W. L. and W. H. Bragg were quick to perceive that experimental simplicity could be achieved by using monochromatic X-radiation, so that d and θ were the only variables in the Bragg equation. Such monochromatic radiation could be obtained by utilizing the characteristic X-ray spectrum of the material of the anticathode of an X-ray tube. The original Bragg method, using an ionization spectrometer, as described in many books, is but rarely used. It is, however, capable of affording the most precise data for intensities of reflection, and has been used in a few laboratories for the most refined work.

With modern improvements in the technique of measuring ionizing radiations, there has been a revival of interest in experimental methods related, in principle, to Bragg's original technique, but using Geiger-Müller counters and electronic measuring apparatus.

(iii) Rotating crystal method. The Bragg method has given place, as the standard procedure, to the rotating crystal method of Rinne, Schiebold and Polanyi (1920). In this, a pencil of monochromatic X-rays (radiation from a copper or iron anticathode; molybdenum, cobalt and chromium K-radiations are also employed) illuminates a small single crystal, which is slowly rotated about a predetermined axis. Successive planes are then brought into reflecting positions, and the reflected beams are recorded photographically—usually on a cylindrical film, surrounding the crystal, so that reflections can be recorded for which θ approaches 90 degrees. If the axis about which the crystal is rotated corresponds with one of the principal crystallographic directions, all the reflections fall on 'layer lines'. The family of planes responsible for each reflection can then be very readily identified: relative intensities can be determined from the photograph. This method, which can be yet further refined by synchronously moving both crystal and film (Weissenberg method), is the most powerful technique for determination of crystal structures.

(iv) Powder method—Debye and Scherrer, Hull (1917). Where the investigation of a single crystal is impracticable (*e.g.* for many

substances obtainable only in a finely divided, although crystalline, state), a polycrystalline specimen may be used, with monochromatic radiation. If, in a polycrystalline material, the crystals are oriented completely at random, some will lie so as to fulfil the Bragg condition for each value of d , and reflections will be recorded for each set of planes. The reflections from one and the same family of planes, in the many crystals contributing to the recorded image, lie on cones, of semi-angle 2θ , which are intersected by a photographic film, in a circular camera. Reflections from planes with similar spacing but different Miller indices are not separated, and for this reason, powder photographs are often not adequate for the complete analysis of crystal structures, except for crystals of the highest symmetry classes. They are, however, very suited for the identification of compounds and for analytical purposes, for the determination of lattice parameters and for the study of the orientation of crystals in metals, etc. Moreover, since substances of simple empirical formula tend to crystallize in the simpler, highly symmetrical lattice types (cubic and hexagonal systems), the powder method has, in practice, found a wide application in the study of inorganic compounds (*e.g.* halides, oxides, etc.) that cannot be obtained in the macro-crystalline state.

The Classification of Crystal Types.—The structures of a very large number of compounds have been determined, so that we are now able to perceive some correlation between the chemical constitution, the physical and chemical properties, and the crystal structure of solids. We may recognize five types of interaction between atoms or molecules, that may serve as cohesive forces, binding them in the regular array of the crystal lattice. These types of interaction are:

- (i) ionic forces—electrostatic forces between ions;
- (ii) homopolar forces—covalent links between atoms;
- (iii) metallic forces;
- (iv) van der Waals forces;
- (v) hydrogen bonds.

(i) In ionic crystals the structure is based upon the regular packing together of ions of the constituent elements, and the lattice forces are the electrostatic attractions between the ions. A very large proportion of inorganic compounds may be classified under this heading, which includes not only the majority of the binary salts, such as NaCl , CaF_2 , but also salts containing radicle ions; thus, in sulphates and carbonates the SO_4^{2-} and CO_3^{2-} ions exist as discrete entities in the lattice. Since ionic forces are undirected in character, we may foresee that the crystalline structure assumed under the influence of ionic forces will be determined chiefly by

geometrical factors, such as the relative size (and with radicle ions, the effective shape) of the ions.

(ii) Homopolar forces between atoms may not only lead to the linking of atoms into small discrete kinetic units (*i.e.* molecules), but may also link together atoms throughout a crystal lattice. In such a case we may think of a crystal as an infinite polymer of the compound in question (contrast with van der Waals forces, below). We know from other evidence—for example, the stereochemistry of organic compounds and of complex salts—that covalent forces are strongly directional in properties, so that in crystals where covalent forces are operative—either within a structural unit or throughout the lattice—the atoms must be disposed in accordance with the valency angles of each element.

(iii) Metallic binding. The properties of metallic crystals may be interpreted on the hypothesis that the valency electrons move, not in orbits determined by the attraction of a single nucleus, as in an isolated atom, but in the periodic field of all the atoms of the lattice, and are, in effect, shared by all the atoms. The effective radii of atoms in metallic crystals, both of elements and of alloys, differ from the ionic radii of the same elements, and are to be identified with the radii of the neutral atoms (covalent radii). It will be found difficult to draw a clear line of demarcation between metals, alloys, intermetallic compounds and typical homopolar compounds. We may note, however, that in the true metals the lattice forces are undirected. In consequence, the atoms, in metallic elements, tend to arrange themselves in one or other of the two ways of achieving closest packing of equal spheres—the hexagonal close-packed or the face-centred cubic arrangements. In each of these, every atom is in contact with 12 nearest neighbours, as a section of the hexagonal close-packed lattice parallel to (0001), and of the face-centred cubic lattice parallel to (111) will show.

(iv) van der Waals forces, the residual forces between electrostatically neutral molecules, manifested in all three states of matter, serve as cohesive forces where a crystal lattice is built up from individual molecules, identical with those capable of existing in the gaseous phase. These forces are weak compared with the electrostatic lattice forces of ionic crystals, or covalent binding forces. They are, accordingly, relatively easily overcome—for example, by thermal agitation. For this reason, compounds forming *molecular crystals* are usually soft, are fusible at low temperatures and, if the molecular weight be not too high, are frequently volatile and readily soluble in non-polar solvents. Furthermore, since vaporization or dissolution of the crystal in a solvent merely disperses pre-existing molecules, the typical molecular properties—absorption spectrum,

magnetic susceptibility, etc.—are essentially the same in the crystalline and the disperse state. This may be contrasted with the ionic and homopolar crystal types, which must be depolymerized in order to furnish the individual molecules that compose their vapours. Molecular crystals are typified by the numerous compounds of organic chemistry, but among inorganic compounds this type of solid is less frequently encountered. Rhombic and monoclinic sulphur, both built up of S_8 molecules, P_4O_6 , SnI_4 may be cited as examples. It will be noticed in the descriptive sections of the book that a number of instances of allotropy or polymorphism can be traced to the crystallization of the same element or compound both in a molecular lattice and in infinitely polymerized form, with homopolar bonds running throughout the lattice. The structures of the two forms of antimony (iii) oxide—senarmontite, Sb_4O_6 , and valentinite, $(Sb_2O_3)_\infty$ —and the allotropy of sulphur trioxide and phosphorus (v) oxide illustrate this phenomenon.

(v) Hydrogen bonds. The hydrogen atom may, under certain circumstances, form fairly strong bonds with two atoms simultaneously. This property arises from the vanishingly small size of the hydrogen ion, the bare proton, which confers on it (a) very high polarizing power and (b) a co-ordination number of 2 (see below, p. 75). The polarizing power is so high that the bare proton has no free existence as a chemical entity in condensed systems, but the hydrogen atom of a $>NH$, $-OH$ or HF group (i.e. a hydrogen atom bound to an atom of high electron affinity) can polarize and bind a second N, O or F atom. Such a *hydrogen bond* is well typified by the HF_2^- anion, which exists as a structural unit in KHF_2 , etc. The binding is usually said to be essentially ionic in character, giving the structure $[F^- H^+ F^-]$, though resonance between the equivalent structures $[F^- H-F]$ and $[F-H F^-]$ might also occur. Whatever the precise mechanism of binding, the existence of such a link is attested by the abnormally close approach of the two fluorine atoms concerned; the $F-F$ distance in KHF_2 is 2.26 Å, compared with twice the radius of the F^- ion, = 2.72 Å. It is this contraction of interatomic distances, indeed, that provides some of the clearest evidence for the existence of hydrogen bonds. Where hydrogen bonds are formed with O, N or F atoms already linked to hydrogen (e.g. between two $-OH$ groups), the contraction of interatomic distances and the bond strength are both diminished. As a cohesive force, hydrogen bonds are intermediate in strength between the van der Waals and the covalent forces.

The nature of the cohesive forces in a crystal cannot, generally speaking, be unambiguously inferred from the structure of the crystal alone. Physical properties which depend directly on the

cohesion—hardness, solubility, fusibility and volatility—or on the nature of the structural units—*e.g.* electrical conductivity—must be considered also.

As was stated above, the only direct conclusion to be drawn from crystal analysis is the *position* of every atom within the crystal lattice; all else is inference. Since the forces of interaction between atoms fall off rapidly with distance, we can, however, recognize those atoms that are linked by predominantly covalent forces, by reason of their closer approach to each other than to their other neighbours. According as the interatomic distances reveal the existence of finite complexes of atoms, or of atoms linked in infinite extension in one, two or three dimensions, we may, following A. F. Wells, classify all observed crystal structures as set out in Fig. 14. We may then consider the factors that determine the structure observed for any substance, and the relation between structure and properties.

Under mechanical stress (*e.g.* shear stresses), or through thermal agitation, the weakest binding forces of the lattice are, naturally, most readily overcome. For this reason, crystallographic planes across which only van der Waals forces operate constitute planes of ready cleavage, and structures built up from infinite one- or two-dimensional complexes crystallize naturally in a fibrous or a platy habit respectively. The influence of the strength of the cohesive forces upon the mechanical and physical properties of a compound may be seen by comparing, *e.g.* NaF with MgO, both being ionic compounds with the NaCl structure. The former melts at 992°C . and has hardness 3.2; corresponding data for MgO are 2800° and 6.5.

The Structures of the Elements.—In the lattice of a crystalline element we have only the packing of like atoms to consider. The geometrical factors that largely determine the structure of compounds (*see below*) are therefore lacking, and the structure assumed by elements is determined solely by the binding forces between their atoms.

(a) Where no directed forces are involved, the whole lattice constitutes an infinite three-dimensional complex (Fig. 14) so that the atoms tend to adopt the close-packed structures in which each has the greatest possible number (12) of nearest neighbours. Such is the case with the inert gases, between the atoms of which van der Waals forces are the only interactions. These elements accordingly crystallize in face-centred cubic lattices, with low melting points and high vapour pressures owing to the smallness of the cohesive forces.

In contrast with this, and evidencing the operation of directed

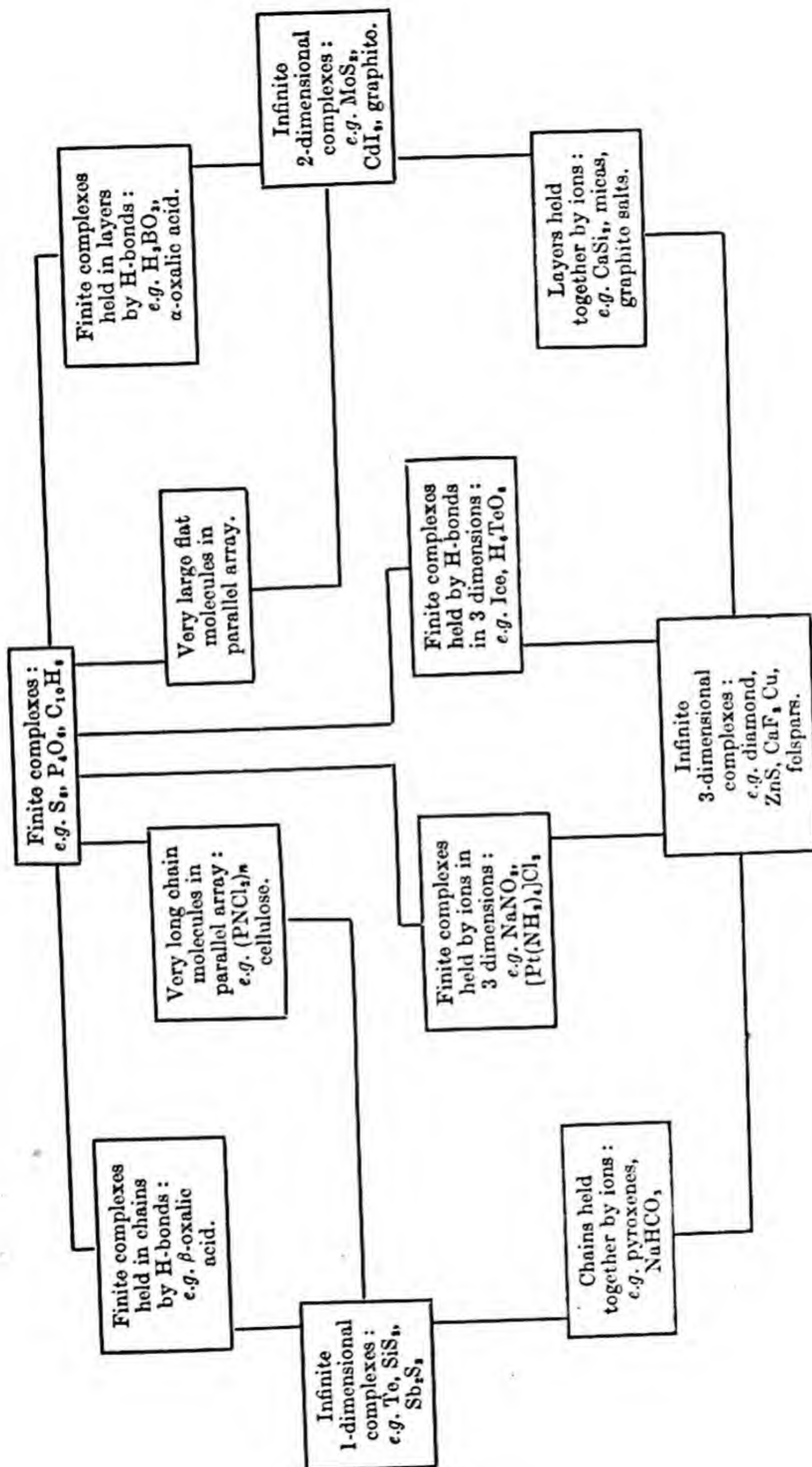


FIG. 14.

homopolar bonds, we have in the diamond (also in silicon, germanium and grey tin) the formation of 'giant molecules'. Each atom can form four covalencies, and is linked to four nearest neighbours, even though the infinite complex so formed has a relatively open structure. We may note, however, a trend from the purely homopolar towards the metallic type of linkage, shown by the progressive change in cohesive and electrical properties, as we descend the 4th group of the periodic table.

The third type of infinite three-dimensional complex we find in the metallic elements, the operation of undirected metallic forces resulting in close-packed structures. An ideal metal would therefore crystallize either in the face-centred cubic structure, or in the hexagonal close-packed structure with $c/a = 1.633$; many do so, but a number—particularly transition metals and metals with large, easily deformable atoms (V, Cr, Mo, α -Fe, W, Ba, Eu and the alkali metals)—crystallize in the slightly more open body-centred cubic structure. We may notice a transition, also, from the ideal metallic lattice towards the development of homopolar bond character, as for example in the sequence

Cu face centred cubic.

Zn hexagonal, not quite close packed, with $c/a = 1.86$; *i.e.* a distinct drawing together into layers.

Ga unique rhombic structure, with distinct incipient segregation of atoms into Ga_2 molecules (*cf.* melting-point).

Ge diamond structure; binding largely homopolar.

There is a similar and very striking gradation running right across the period Ag-Cd-In-Sn-Sb-Te-I.

(b) An atom of an element of the n^{th} group ($4 \leq n \leq 7$) of the periodic table can form $(8 - n)$ covalent bonds. Hence, where homopolar forces determine crystal structure, it is not surprising to find that each atom has $(8 - n)$ nearest neighbours. This has already been exemplified by the diamond structure of the group IV elements. With the elements of group V the rule leads to the association of every atom with three nearest neighbours. One structure satisfying this condition is that found in grey arsenic, antimony and bismuth, wherein the atoms are drawn together into infinite two-dimensional complexes—puckered sheets of trigonal symmetry. A progressive transition towards the metallic type is again perceptible, but all these elements are notably imperfect in metallic character.

(c) The $(8 - n)$ rule implies that each atom of a group VI element should have two nearest neighbours in the lattice. The only infinite complex fulfilling this condition is the chain structure which we find in the crystal lattice of selenium and tellurium. As

with the sheet structures of As, Sb and Bi, the residual forces between adjacent chains seem to be metallic in character. We may note that with sulphur, while the $(8 - n)$ rule applies, the tendency to form chains is apparent only in the allotropy of the liquid ($S_8 \rightarrow S_n$ transformation).

(d) We have, finally, those elements that form finite complexes. The halogens, in conformity with the $(8 - n)$ rule, build up their crystal lattices from diatomic molecules, whilst elements of higher valency can also conform with the rule by the formation of closed groups of atoms; we thus have the S_8 ring molecule of sulphur, and the tetraatomic tetrahedral molecule found in white phosphorus and (presumably) in yellow arsenic. The formation of molecular lattices, with their concomitant physical properties, will be found to be confined to the typically non-metallic elements.

The Structures of Binary Compounds.—Under this heading it is convenient to consider first the predominantly electrovalent compounds formed by pairs of elements of widely different electronegativity. In such compounds we may suppose the crystal to be built up from atoms that are distinguishable only in respect of their different sizes and the magnitude and polarity of their ionic charges.

The binary compounds of the elements crystallize, in many cases, in simple structural types, so that the spacing between the principal planes of the crystal is directly related to the distance between neighbouring atoms or ions. For example, in the sodium chloride structure, common to many of the compounds of the type MX , the interatomic distance $M-X$ is half the length of the edge of the cubic unit cell. In such a series of compounds of similar structure, the ions behave roughly as though they were spheres of definite and constant radius, the observed distances being equal to the sum of the radii of the cations and anions respectively. Thus if we compare the series of sodium and potassium halides, the difference between the interatomic distances $Na-X$ and $K-X$ (where $X = F, Cl, Br, I$) is almost the same for each pair. Closer examination shows that this is only approximately true, and unless certain correcting factors are introduced, comparison is possible only between compounds of similar structure, involving ions of like valency. Commensurable data are thereby obtained, so that if the true radius of any one ion were known, the radii of other ions could be deduced. A self-consistent set of ionic radii, with a quasi-theoretical basis, has been drawn up in this way (Table 1) on the next page.

Table 1
Ionic Radii, in Å

<i>A sub-group elements.</i>								
- 3	- 2	- 1	+ 1	+ 2	+ 3	+ 4	+ 5	+ 6
		H	Li	Be	B			
		1.53	0.60	0.31	0.20			
N	O	F	Na	Mg	Al	Si		
1.71	1.40	1.36	0.95	0.65	0.50	0.41		
P	S	Cl	K	Ca	Sc	Ti	V	Cr
2.12	1.84	1.81	1.33	0.99	0.81	0.68	0.59	0.52
As	Se	Br	Rb	Sr	Y	Zr	Nb	Mo
2.22	1.98	1.95	1.48	1.13	0.93	0.80	0.70	0.62
Sb	Te	I	Cs	Ba	La	Ce		
2.45	2.21	2.16	1.69	1.35	1.15	1.01		
<i>B sub-group elements.</i>								
			Cu	Zn	Ga	Ge	As	
			0.96	0.74	0.62	0.53	0.47	
			Ag	Cd	In	Sn	Sb	
			1.26	0.97	0.81	0.71	0.62	
			Au	Hg	Tl	Pb	Bi	
			1.37	1.10	0.95	0.84	0.74	
					Tl ⁺	Pb ⁺⁺		
					1.44	1.21		
<i>Transition metal cations.</i>								
	Ti ³⁺	V ³⁺	Cr ³⁺	Mn ²⁺	Fe ³⁺			
	0.69	0.66	0.64	0.62	0.60			
				Mn ²⁺	Fe ²⁺	Co ²⁺	Ni ²⁺	
				0.80	0.75	0.72	0.69	

From such a set of ionic radii it is possible to frame certain generalizations. (i) The ionic radius of any cation is smaller than the radius of the neutral atom of the same element, whereas the radius of an anion is greater. (ii) For any one element, the radius decreases progressively with increase in the cationic charge—*i.e.* as electrons of the highest quantum number (largest orbital radius) are stripped off, and the average tightness of binding is increased, *e.g.*

Pb 1.46 Å	Pb ²⁺ 1.21 Å	Pb ⁴⁺ 0.84 Å
Mn 1.18 Å	Mn ²⁺ 0.80 Å	Mn ³⁺ 0.62 Å
		Mn ⁴⁺ 0.52 Å (Mn ⁷⁺ 0.46 Å)

It is an important consequence of this rule that highly charged cations are very small, and have high polarizing power. The importance of this for the transition from electrovalent to covalent bonding was discussed in Chapter III. (iii) In any series of iso-electronic ions, the radius decreases rapidly from element to element as the charge increases. The corresponding increase in radius with increase in negative charge is rather less striking. (iv) In the transition series, where ions of the same valency may be formed by a series of consecutive elements, there is always a progressive decrease in radius as the atomic number of the ion increases.

This contraction is particularly important in the long series of the rare earths, the radius of the Ce^{3+} ion being 1.18 Å and that of the Lu^{3+} ion 0.99 Å. In consequence of this, the elements immediately following the rare earths are no larger in atomic radius and ionic radius than their congeners of the preceding Long Period, and we find the abnormally close similarity between members of the pairs Zr-Hf and Nb-Ta. This shrinkage has been called the Lanthanide Contraction.

Since the forces between ions are not spatially directed, the structures assumed by ionic compounds are determined chiefly by the relative numbers of each kind of ion, and by their relative sizes. In order to attain maximum stability, compact structures are usually built up, in which every ion is surrounded by as many ions of opposite sign as is possible. This number, the number of nearest neighbours, is known as the *Goldschmidt co-ordination number*, and is determined by the ratio of the ionic radius of the cation A to the ionic radius of the anion X, i.e. by $R_A : R_X$. For any particular geometrical arrangement of the larger ions (which, as has been seen, are usually the anions) about the cations there is a lower limiting value of $R_A : R_X$ below which the larger ions would be in contact with each other, but not with the ion of opposite sign. Greater stability would then be achieved if another geometrical arrangement, of lower co-ordination number, were assumed. We can calculate geometrically (Fig. 15) the limiting values of the radius ratio, at which the changes in co-ordination number may be expected to occur. These are set out in Table 2.

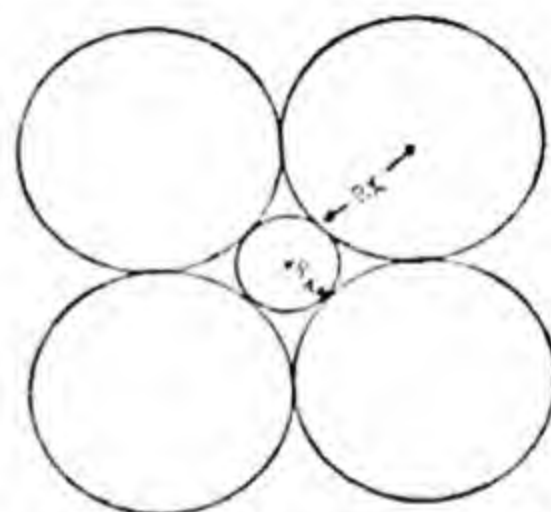


FIG. 15.—Illustrating the limiting ratio for fourfold square co-ordination.

Table 2
Limiting Radius Ratios

Radius ratio $R_A : R_X$	Co-ordination no.	Geometrical arrangement
1	12	Close packing
1-0.732	8	Corners of cube
0.732-0.414	6	Corners of octahedron
0.414-0.22	4	Vertices of tetrahedron
0.732-0.414	4	Corners of plane square
0.22-0.15	3	Corners of triangle
Less than 0.15	2	Linear

In a simple binary compound AX, each kind of ion necessarily

has the same co-ordination number. Thus, in the sodium chloride structure (Fig. 16), the arrangement can be described as one of 6 : 6 co-ordination. Cæsium chloride is not truly isomorphous with the halides of the other alkali metals. The radius ratio $R_{Cs^+} : R_{Cl^-}$ is 0.93, so that in accord with the above table, the CsCl lattice is

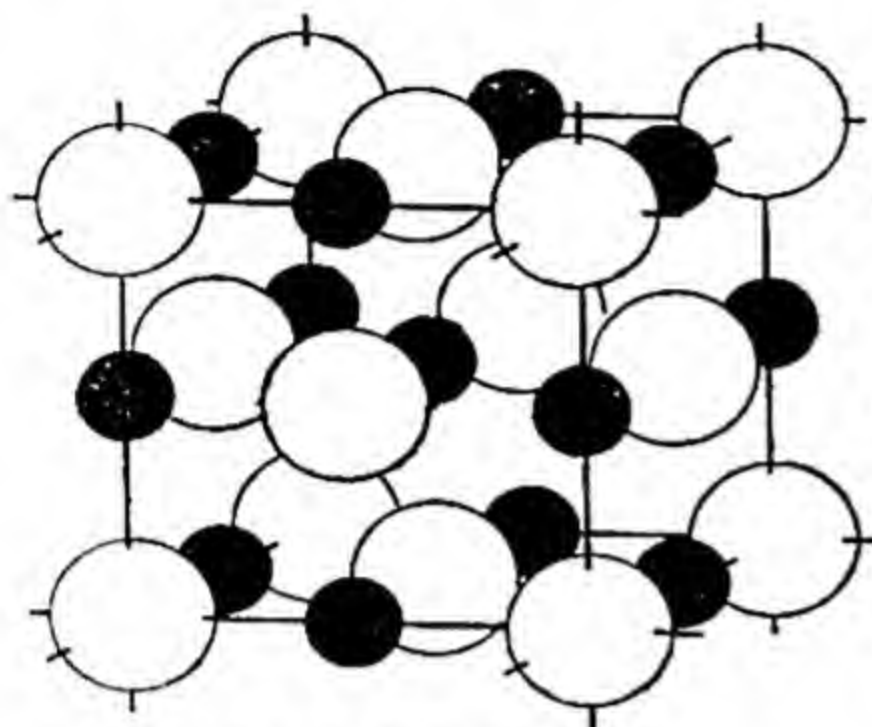


FIG. 16.—NaCl Structure :
6 : 6 co-ordination.

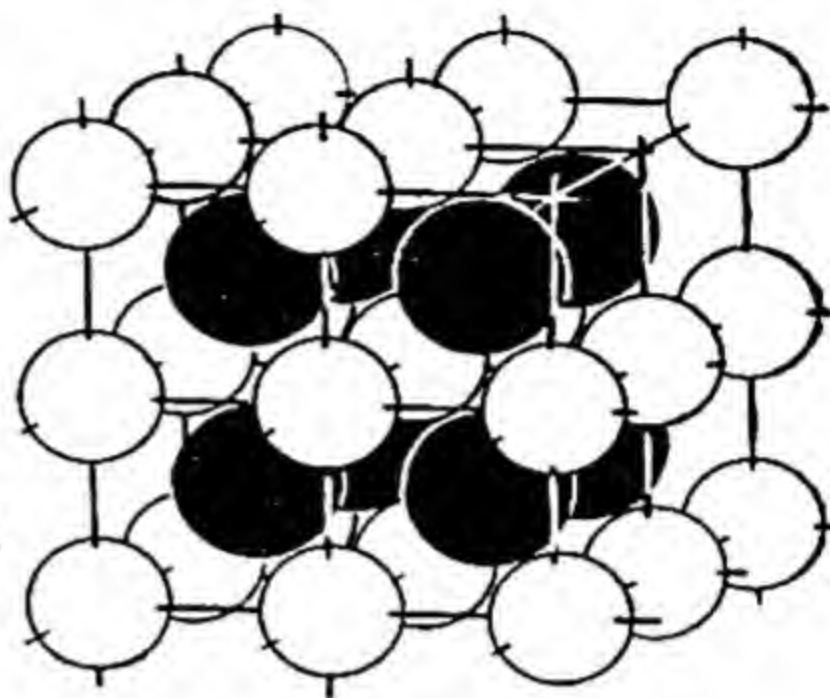


FIG. 17.—CsCl Structure :
8 : 8 co-ordination.

based on 8 : 8 co-ordination (Fig. 17). In compounds of the type AX_2 , the co-ordination number of the ion A must be twice that of the ion X. The structure as a whole is then determined by the co-ordination around the smaller ion. Examples of the most common types of structure resulting from different values of the radius ratio in AX_2 compounds are :

SiO_2	$R_A : R_X = 0.293$	Co-ordination 4 : 2	Cristobalite structure (Fig. 18)
TiO_2	0.486	6 : 3	Rutile structure (Fig. 19)
CaF_2	0.73	8 : 4	Fluorite structure (Fig. 20)

In all these 'type structures', the arrangement is symmetrical about both kinds of ion, as indeed it must be if only undirected electrostatic forces are involved. The actual number of different types of structure exhibited by ionic compounds is thus limited, and the arrangements already referred to will be repeatedly encountered.

Even where radicle ions are involved, the foregoing considerations are valid, even though their application is less clear cut. Thus, calcium carbonate is dimorphous, and crystallizes as calcite and aragonite, each of which is a member of a well-known isomorphous series. It appears that the radius of the Ca^{2+} ion must be close to the critical value for the change over from the calcite type to the aragonite type of structure, because the carbonates of all the bivalent metals (Mg, Mn, Fe, etc.) having ionic radii less than that of the Ca^{2+} ion are isomorphous with calcite, while the carbonates

of metals with greater ionic radius (Sr, Ba, Pb) are isomorphous with aragonite. The nitrates $M^I\text{NO}_3$, and the borates $M^{III}\text{BO}_3$, have the same structures, and the change of one type to another

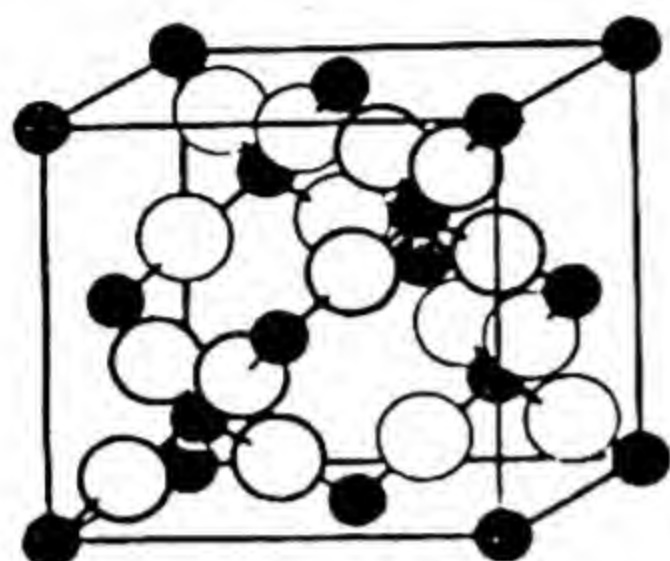


FIG. 18.— SiO_2 cristobalite structure : 4 : 2 co-ordination.

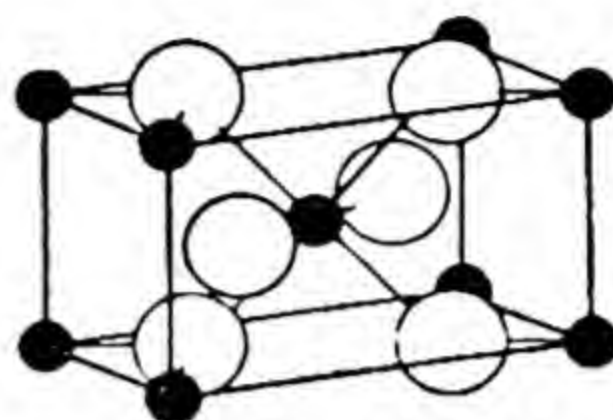


FIG. 19.— TiO_2 rutile structure : 6 : 3 co-ordination.

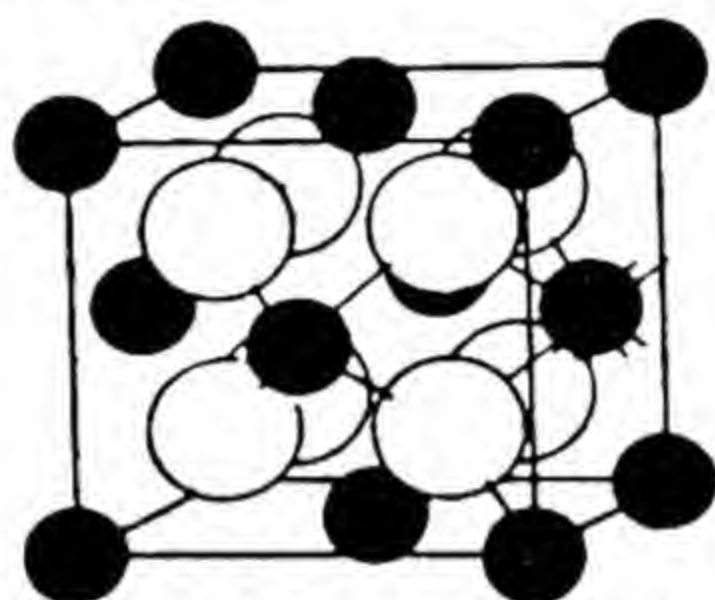


FIG. 20.— CaF_2 fluorite structure : 8 : 4 co-ordination.

occurs at about the same value of the radius ratio $R_M : R_{\text{O}^{2-}}$ (Table 3). As is discussed below, it is not really permissible to think of nitrates, carbonates, etc., as having O^{2-} ions as constituents of the lattice. The XO_3 anions cited are covalent complexes of atoms, having the same shape and size; it is not unreasonable, however, to take the size of the O^{2-} ion as a measure of the way these triangular anions pack about the metallic cations.

Table 3

Calcite structure . . .	LiNO_3 0.34	MgCO_3 0.47	ScBO_3 0.60
	NaNO_3 0.54	ZnCO_3 0.50	InBO_3 0.59
		CaCO_3 0.67	YBO_3 0.68
Aragonite structure . . .	KNO_3 0.76	CaCO_3 0.67	LaBO_3 0.79
		SrCO_3 0.75	
		BaCO_3 0.87	

We have seen on a previous page that cations are, for the most part, considerably smaller than anions. In various important

classes of compounds—the silicates, borates, heteropolyacids, etc.—oxygen ions O^{2-} are the ions that principally determine the structure. The co-ordination numbers of the principal metallic ions towards oxygen are set out in Table 4.

Table 4
Co-ordination Numbers of Ions in Oxide Structures

Ion	Radius	$R_A : R_{O^{2-}}$	Co-ordination number	
			Predicted	Observed
B^{3+}	0.24A	0.18	3	3 and 4
Be^{2+}	0.34	0.25	4	4
Si^{4+}	0.39	0.30	4	4
Ge^{4+}	0.44	0.33	4	4
Al^{3+}	0.57	0.41	4 or 6	4 and 6
Ti^{4+}	0.64	0.48	6	6
Mo^{6+}	0.64	0.48	6	6
V^{2+}	0.65	0.49	6	6
Sn^{4+}	0.74	0.56	6	6
Mg^{2+}	0.78	0.58	6	6
Li^{+}	0.78	0.58	6	6
Sc^{3+}	0.83	0.63	6	6
Zr^{4+}	0.87	0.65	6	6 and 8
Na^{+}	0.98	0.74	8	8
Ce^{4+}	1.02	0.77	8	8
Ca^{2+}	1.06	0.80	8	8
Th^{4+}	1.10	0.83	8	8
K^{+}	1.33	1.00	8 or 12	6, 8, 10, 12

The Formation of Layer Lattices.—As was seen in Chapter I, the spherical distribution of electric charge on an ion would be distorted by the action of ions of opposite sign, this polarizability being particularly great for the anions of large radius, such as the S^{2-} and I^{-} ions. In the crystal lattice, polarization can have the effect of drawing the atoms into sheets, in such a way that the deformed ions are no longer symmetrically surrounded by the ions of opposite sign. Such a structure is known as a *layer lattice*.

The occurrence of this effect is typified by the cadmium halogenides. CdF_2 is a truly ionic compound, because the F^{-} ion is but little polarizable; the salt crystallizes, with 8 : 4 co-ordination, in the fluorite structure. On account of the much greater ionic radius of the I^{-} ion, CdI_2 exhibits a structure based on 6 : 3 co-ordination, but not the rutile structure typical of truly ionic compounds. The difference arises from the high polarizability of the I^{-} ion. Whereas each Cd^{2+} ion is at the centre of an octohedron of I^{-} ions, the three

Cd^{2+} ions with which each I^- ion is associated lie *all on the same side* of the iodine ion (Fig. 21). The cations, and the anions directly

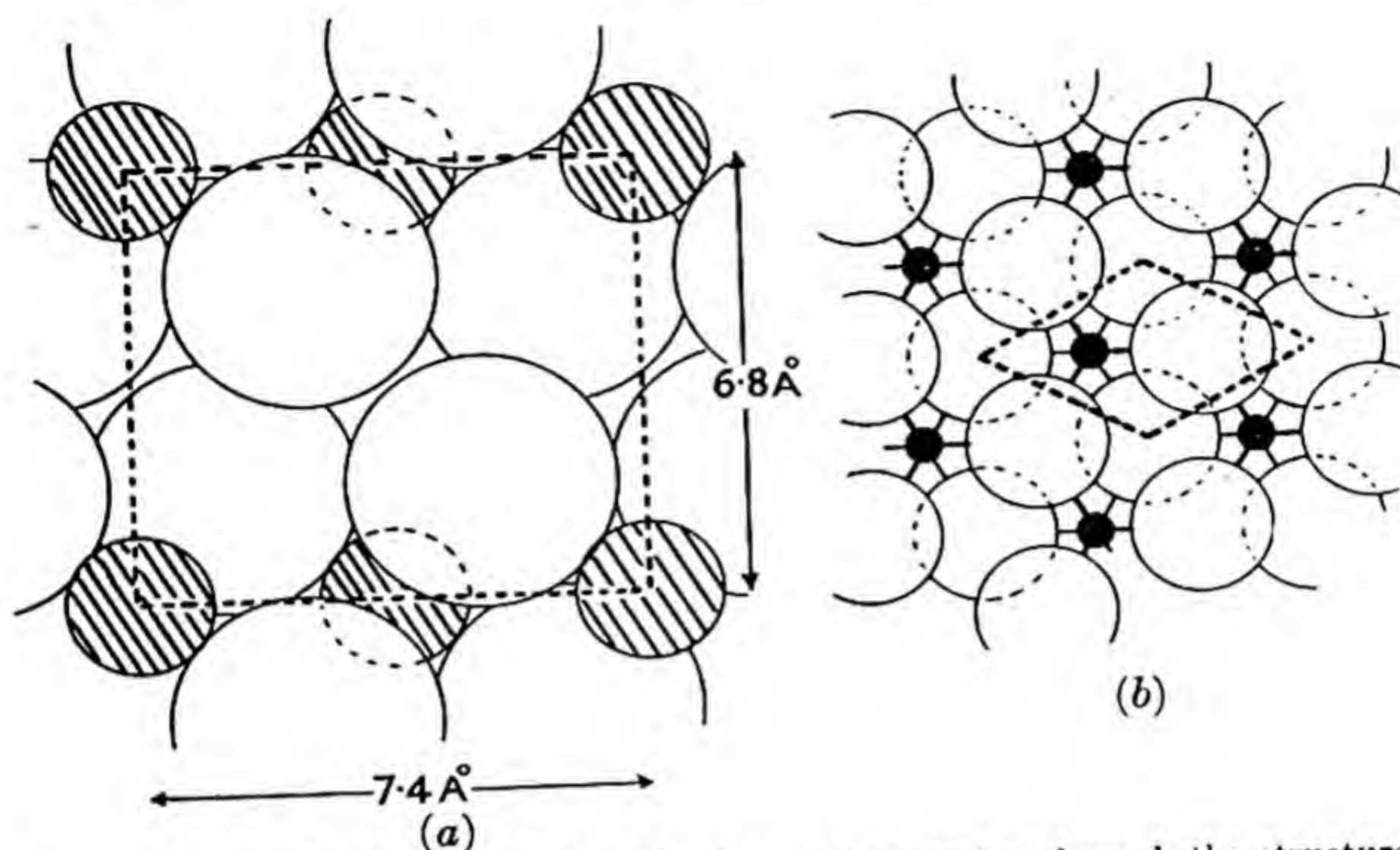


FIG. 21.—The cadmium iodide layer lattice. (a) A section through the structure. (b) A plan view of one sheet. The dotted lines mark the outline of one cell.

linked to them, thus form layers, each of which is electrically neutral. If we trace the sequence of ions along a line perpendicular to these sheets, we find the arrangement represented diagrammatically as in Fig. 22, in which the successive layers contain only I^- ions, or only Cd^{2+} ions. The forces between sheets of anions and sheets of cations are very strong compared with the residual forces between contiguous sheets of iodide ions. Each such 'sandwich' is, in fact, more tightly bound together than are the

	I	I	I	I	I	I	(1)
	Cd	Cd	Cd	Cd	Cd	Cd	(2)
	I	I	I	I	I	I	(3)
cleavage								
	I	I	I	I	I	I	(4)
	Cd	Cd	Cd	Cd	Cd	Cd	(5)
	I	I	I	I	I	I	(6)
cleavage								
	I	I	I	I	I	I	(7)
	Cd	Cd	Cd	Cd	Cd	Cd	(8)

Layers 1, 3, 4, 6, 7, 9, etc., consist only of I^- ions.
Layers 2, 5, 8, etc., consist only of Cd^{2+} ions.

FIG. 22.—Cadmium iodide type layer lattice. Diagrammatic representation of the succession of 'sandwiches'.

ions of a purely ionic lattice, and can be regarded as a two-dimensional giant molecule. Since the forces between adjacent composite layers are only the van der Waals forces, crystals of this kind accordingly show a pronounced cleavage parallel to the sheets. The line in Fig. 22 represents such a cleavage plane.

Layer lattice structures are invariably formed by compounds of the types AX_2 and AX_3 whenever the polarization effect is sufficiently high. Thus, the iodides of all the bivalent metals, and the bromides and chlorides of all metals with an ionic radius smaller than that of the Ca^{2+} ion, crystallize in this way (though it should be noted that the cadmium iodide type is not the only possible layer lattice arrangement). Only the fluorides are, invariably, true ionic compounds. That it is a matter of polarization, and not of the relative size of anions and cation, may be perceived by comparing the fluorides of the metals with the hydroxides. The hydroxide ion, OH^- , is not very different in radius from the F^- ion. Intrinsically, however, the OH^- ion is dipolar in character; the distribution of electric charge on the ion is not spherically symmetrical, and the ion is therefore very polarizable. All hydroxides of the types $M(OH)_2$ and $M(OH)_3$ form layer lattices, irrespective of the radius of the ion M . In these latter compounds, moreover, the two-dimensional giant molecules are united by fairly strong forces between the OH^- ions of adjacent layers (so-called *hydroxyl bonds*). It is to this property that the insolubility of the hydroxides can probably be traced.

Adamantine Compounds.—In the compounds of general formula AX formed between the metalloids (Se, Sb, etc.) and the metals of the B sub-groups (Zn, Ga, etc.) polarization effects

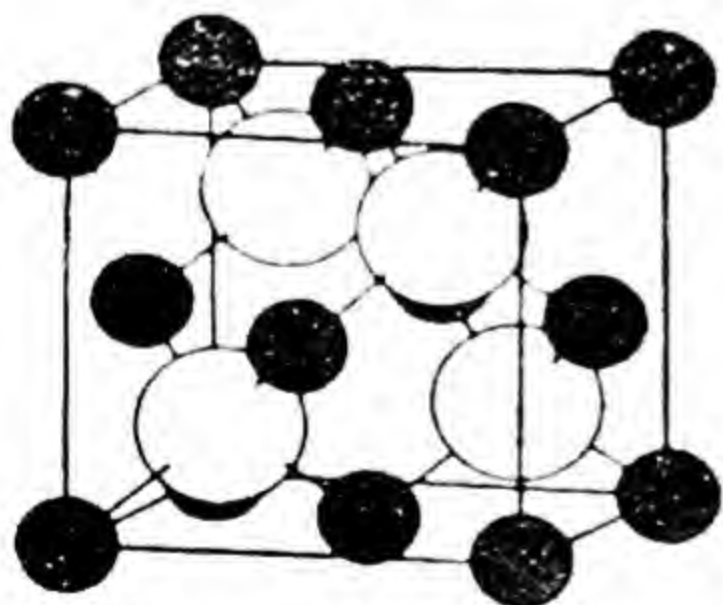


FIG. 23.—Zinc blende structure :
4 : 4 co-ordination.

operate in such a way that these are homopolar compounds, rather than ionic. The typical compound is zinc sulphide, which in both its crystalline forms, zinc blende (or sphalerite) and wurtzite, forms three-dimensional giant molecules. In both, the arrangement of atoms is essentially that of the diamond (Fig. 23), with half the atomic positions occupied by zinc atoms, half by sulphur. The essence of this structure is that every atom is linked to its four neighbours by covalent bonds,

but the eight electrons thereby involved in bond formation are not provided equally by the zinc and sulphur atoms. All six valency electrons of the sulphur, and the two valency electrons of

the zinc, are contributed to the crystal lattice. The point of greatest interest is that the formation of such an adamantine crystal occurs whenever the two constituent elements possess, between them, eight valency electrons. Further, for a series of compounds in which the sum of the atomic numbers of the two elements is the same throughout, the actual interatomic distance is practically identical with that found in the corresponding Group IV element possessing the true diamond structure (Table 5).

Table 5

Compound	Atomic numbers	Valency electrons	Interatomic distance
AlSb	$13 + 51 = 64$	$3 + 5 = 8$	2.64A
SCd	$16 + 48 = 64$	$6 + 2 = 8$	2.52
CuBr	$29 + 35 = 64$	$1 + 7 = 8$	2.46
ZnSe	$30 + 34 = 64$	$2 + 6 = 8$	2.45
GaAs	$31 + 33 = 64$	$3 + 5 = 8$	2.44
Ge	$(32 + 32 = 64)$	$(4 + 4 = 8)$	2.44

This formation of adamantine compounds where the above condition is fulfilled is sometimes referred to as the *Grimm-Sommerfeld Rule*. In the compounds of the transition metals with the chalcogens and metalloids, although this rule does not apply, we find again that the compounds are not salts, but homopolar in character. The formulæ of such compounds do not follow the ordinary valency rules, but conform, for the most part, to a few very simple types. Thus we have AX compounds such as NiAs, PtSb; AX_2 compounds, FeS_2 , $PtAs_2$, $FeAsS$. This at once suggests that their composition is determined primarily by the geometry of crystal structure. Further, all the valency electrons of the elements are not employed in bond formation, with the result that the compounds are frequently semi-metallic in character. One can, indeed, trace a continuous gradation in properties between these substances and the true intermetallic compounds.

Goldschmidt's Law.—The principles discussed in the foregoing paragraphs are summarized in the statement, formulated by V. M. Goldschmidt (1926), that the crystalline structure of a solid compound is determined by the relative numbers, the relative radii, and the polarizability of the atoms of the constituent elements.

Ternary Compounds.—Amongst the ternary compounds of the elements we may draw a distinction, on the basis of Fig. 14, between those compounds in which the crystal structure reveals the existence of discrete anionic radicles, and those in which the whole crystal

structure constitutes an infinite three-dimensional complex. Thus, amongst the oxygen compounds there are, on the one hand, the salts of the oxy-acids, and on the other hand the multiple oxides $A_xB_yO_z$, in which the elements A and B play an essentially similar role. The type of structure adopted by a particular compound depends on the difference in magnitude of the polarizing effects and electronegativities of the elements A and B.

Discrete anionic groups are formed when the forces of polarization are very large—*i.e.* when a purely ionic structure would involve cations of very high charge. Where the binding forces within the anionic group are essentially covalent, the shape of the group is determined by the directional properties of the bond orbitals concerned. The packing of anions and cations into a three-dimensional structure is governed by both the shape and the size of the ions. The shapes of some of the more common complex anions are shown in Table 6 below.

Table 6

A_2, AX		O_2^{2-}, C_2^{2-}, CN^-
A_3, AX_2, AXY	Linear	$N_3^-, CNO^-, CNS^-, [Ag(CN)_2]^-$
	Angular	ClO_2^-, NO_2^-
AX_3	Planar	NO_3^-, CO_3^{2-}
	Pyramidal	$ClO_3^-, BrO_3^-, SO_3^{2-}, PO_3^{3-}, AsO_3^{3-}$
AX_4	Tetrahedral	$BF_4^{2-}, PO_4^{3-}, SO_4^{2-}, ClO_4^-, MnO_4^-$
	Planar	$PdCl_4^{2-}, PtCl_4^{2-}, [Ni(CN)_4]^{2-}$
AX_6	Octohedral	$SiF_6^{2-}, PtCl_6^{2-}$

There are, however, many compounds commonly written as salts, in which there is no justification for singling out any one element as the central atom of a radicle anion.

To this type belong a number of very important classes of inorganic compounds—in particular, the oxygen compounds ABO_3 and AB_2O_4 . The former class, provided the radii of the cations of the metals A and B are such as to conform reasonably well with the geometry of the arrangement, crystallize in the structure of calcium titanate, $CaTiO_3$, *perovskite* (Fig. 24). In this structure, each atom of B is co-ordinated with 6 oxygens, each atom of A with twelve. It can easily be worked out that for such an arrangement, ideally, $R_A + R_O = \sqrt{2}(R_B + R_O)$; actually there appears to be a certain measure of tolerance, and the perovskite structure is found to be that of a wide variety of compounds which fulfil the condition that $z_A + z_B = 6$. Thus, $Na^I Nb^V O_3$, $Ca^{II} Zr^{IV} O_3$, $Y^{III} Al^{III} O_3$ all form the perovskite lattice. So also does $K^I Mg^{II} F_3$, which fulfils the same essential conditions. It should be noted that for the case $A = B$ the geometrical condition can no longer be fulfilled. In

fact, the A_2O_3 oxides formed from cations of small radius crystallize like Al_2O_3 and Fe_2O_3 ; the oxides of trivalent metals with large cations possess the entirely different rare earth oxide structure.

A second important group of multiple oxides is that of the *spinel*s, AB_2O_4 , which (cf. the condition for assuming the perovskite structure) are formed whenever the charge on the cations totals eight units. Once again, there is no anionic radicle in these compounds.

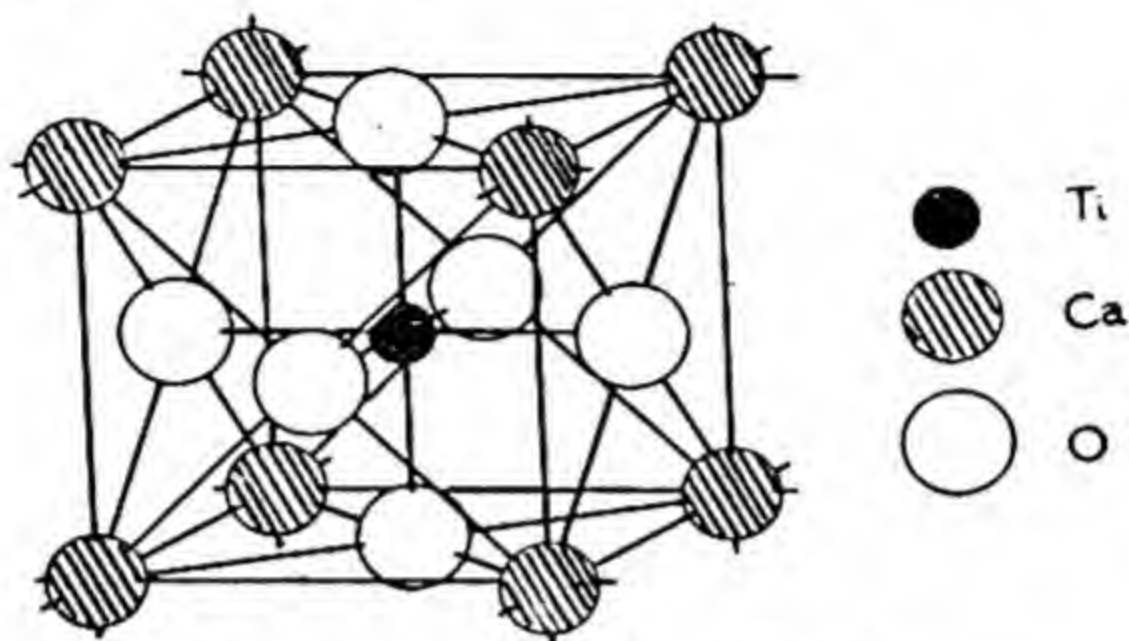


FIG. 24.—Perovskite structure.

Although, from the geometry of the structure, the atom A is surrounded by 4 oxygen atoms, and each atom of B by six oxygen atoms, we cannot justifiably regard spinel itself, $MgAl_2O_4$, either as $Mg[AlO_2]_2$ or as $Al_2[MgO_4]$: the element A may be either more or less electropositive than element B without affecting the assumption of the spinel structure, as may be seen by inspection of Table 7 below. This table shows how the structure occurs with mixed oxides of various formal types provided the condition as to total charge is fulfilled. It will be seen that the M_3O_4 oxides of the transition metals belong to this category.

Table 7

Compounds with Spinel Structure

$AO + B_2O_3$
 $ZnAl_2O_4$
 $MgFe_2O_4$
 $FeFe_2O_4$
 $MgCr_2O_4$
 FeV_2O_4
 $MgIn_2O_4$
 $MnCr_2S_4$
 $CuCo_2S_4$

$2BO + AO_2$
 $TiMg_2O_4$
 $SnMg_2O_4$
 $GeNi_2O_4$
 $TiCo_2O_4$

$BeLi_2F_4$

Water of Crystallization.—It is familiar that many salts crystallize from aqueous solution as hydrates. Both on systematic chemical grounds and as a result of the determination of the

constitution of solid salt hydrates, we may distinguish two distinct functions that can be fulfilled by the water of crystallization.³

(A) In the first place, the water may be co-ordinated to the cation of the salt, not only in the crystallographic sense, but to form a co-ordinated complex ion in the sense of Werner's theory. Thus, in the salts $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$, we have actually the salts of complex aquo-cations— $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$, $[\text{Ni}(\text{H}_2\text{O})_6]\text{SO}_4 \cdot \text{H}_2\text{O}$, $[\text{Be}(\text{H}_2\text{O})_4]\text{SO}_4$ respectively. The effect of the sheath of water molecules around the rather small metallic ions is, primarily, to increase the ineffective radii, and so to decrease greatly their polarizing power. For example, the radius of the Al^{3+} ion is 0.57 Å, and the polarizing effect of the ion is so high that the aluminium halogenides are non-electrolytes in the fused state. The hydrated cation $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$, which exists in $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, $\text{AlBr}_3 \cdot 6\text{H}_2\text{O}$, etc., forms an octohedral complex ion with an effective radius of about 3.3 Å, larger, in fact, than the SO_4^{2-} ion. This complex ion is accordingly able to enter into simple, unpolarized ionic structures.

Consideration shows that the cohesion of complex ions of this type must arise from the manner in which the water molecules are polarized by the metallic cations. One consequence of this is that it is the metals of small ionic radius, and high ionic charge, that tend to form hydrated salts. The distribution of hydrated salts in relation to the Periodic Table will be found to accord with this generalization, their formation being increasingly favoured as we pass from Group I successively to the second and third groups, whilst within any one group the tendency to the hydration of salts diminishes as, with increase in atomic weight, the ionic radius increases. Further, if the cohesive forces of the complex ion are essentially electrostatic, the co-ordination number of the metal in the aquo-cations should be determined chiefly by a geometrical factor—the relative sizes of cation and water molecule. Both these features can be illustrated by the chlorides of the metals of the second group, which crystallize as the hydrated salts listed in Table 8.

(B) There are many hydrated salts that do not fit into the foregoing class of compounds—for example, the heavily hydrated sodium salts such as $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$. In these, the water molecules play a less significant role, and it seems that, by occupying the interstices of the crystal structure, they serve to improve the packing together of anion and cation. One point of interest is that in the heavily hydrated salts, the water molecules are themselves linked together in the same arrangement, and by the same rather weak forces ('hydroxyl bonds') that make up the

³ See also Chap. VI, p. 190.

structure of ice. The same weak, directed forces may bind the water molecules to the other units, particularly the anions, of the structure, so that the water of crystallization plays a definite part in the cohesion of the whole.

In some instances, however, the function of the water is so unimportant that it can be expelled from the crystal lattice without bringing about any change of structure. This is the case with the

Table 8

	r	C.N.		
Be ²⁺	0.31	4	[Be(H ₂ O) ₄]Cl ₂	Aquo-cations formed.
Mg ²⁺	0.65	6	[Mg(H ₂ O) ₆]Cl ₂	
Ca ²⁺	0.99	6	[Ca(H ₂ O) ₆]Cl ₂	
Sr ²⁺	1.13	6	[Sr(H ₂ O) ₆]Cl ₂	
		—	SrCl ₂ .2H ₂ O	Simple, unhydrated cations in crystal.
Ba ²⁺	1.35	—	BaCl ₂ .2H ₂ O	

typical zeolites, and has as its consequence the behaviour of the partially dehydrated compound as a one-phase system, instead of as a two-phase mixture of hydrate and dehydration product.

It should be noted that very frequently water of crystallization of both types—co-ordinated in aquo-cations, and present as 'structural water' in the crystal lattice—is present in the same compound. Thus, aluminium sulphate, Al₂(SO₄)₃.18H₂O, can be formulated as [Al(H₂O)₆]₂(SO₄)₃.6H₂O.

CHAPTER V

STRUCTURE OF MOLECULES OF INORGANIC COMPOUNDS

A great deal of information on the structure of the molecules of inorganic compounds has been obtained by the application of certain well-established physical techniques. In this chapter it is proposed to review some of the results obtained by the following:

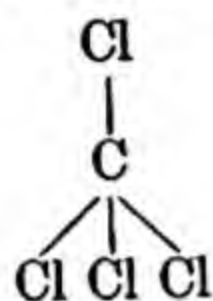
- (a) The diffraction of X-rays and electrons by gases and vapours.
- (b) Spectroscopic methods.
- (c) The measurement of dipole moments.
- (d) Magnetic measurements.

In addition to these methods, and exceeding them in importance, is the use of X-ray diffraction in the study of solids, which has been dealt with in the preceding chapter.

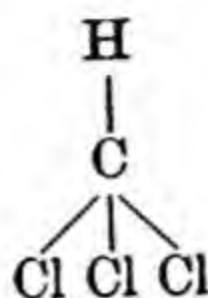
X-Ray and Electron Diffraction by Gases and Vapours.—The theory of X-ray scattering by gases was first developed in 1915 by Debye and Ehrenfest, but it was not until fourteen years later that the subject was studied experimentally. Although this method of studying the structure of gaseous molecules has been largely superseded by the use of electron diffraction, brief reference will be made to some of the classical results obtained.

The scattering of X-rays by gases differs from that by liquids and solids in that the molecules have a completely random orientation, and are practically free from intermolecular forces under normal conditions. The molecules will, however, have certain fixed interatomic distances which are common to them all, and when a beam of X-rays is passed through the gas, the latter will behave in much the same way as a crystalline powder. There will be some molecules so oriented with respect to the incident beam that the waves scattered from the different atoms in any one molecule will reinforce one another in certain directions and interfere in others. A diffraction pattern will therefore be obtained which will consist of a central spot surrounded by a series of haloes, the diameter of the haloes depending, *inter alia*, on the interatomic distances in the molecules examined. The interpretation of the results obtained in the study of X-ray diffraction by gaseous molecules depends on the comparison of the observed radial dis-

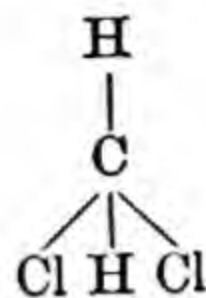
tribution of the intensity of the scattered radiation with that calculated from theoretical relationships, assuming certain inter-atomic distances. The values given below for the distance between chlorine atoms in the halogenated methanes illustrate the type of result obtained.



$$\begin{array}{c} \text{Cl}-\text{Cl} \\ = 2.98-2.99 \text{ \AA.} \end{array}$$



$$\begin{array}{c} \text{Cl}-\text{Cl} \\ = 3.10-3.11 \text{ \AA.} \end{array}$$



$$\begin{array}{c} \text{Cl}-\text{Cl} \\ = 3.18-3.23 \text{ \AA.} \end{array}$$

The distance between adjacent chlorine atoms is increased by substitution of hydrogen in the molecule. In chlorine itself the chlorine atoms are 2.0 Å apart. If silicon tetrachloride is examined in place of carbon tetrachloride, the distance between chlorine atoms is found to be 3.35 Å, *i.e.* since the tetrahedral angle cannot have altered in a symmetrical molecule of this sort, the bond distance between silicon and chlorine must be greater than that between carbon and chlorine.

The possibility of using electron diffraction in the study of molecular structure arises from the property of material particles in motion of behaving as if associated with characteristic waves. The wave-length is given by $\lambda = h/mv$, where h is the Planck constant and m and v are the mass and velocity of the particles. From this relationship the wave-length associated with an electron accelerated by a potential of 1000 volts is 1.2×10^{-9} cm. Normally electrons accelerated through about 50,000 volts are used.

When a beam of accelerated electrons impinges on a stream of gas, scattering occurs, and if the beam then strikes a photographic plate, the image produced is found to consist of an intense central spot surrounded by a series of concentric rings: an effect, in fact, very similar to that produced in X-ray diffraction by gases, and referred to above. The radial intensity distribution is a function of the scattering produced by separate atoms and by pairs of atoms. The theoretical intensity distributions for various assumed molecular models may be calculated and the model which gives the best correspondence between theory and observation is taken as representing the true configuration of the molecules of the gas.

The experimental method may be described in somewhat greater detail. The electron diffraction apparatus is maintained at a very low pressure ($< 10^{-5}$ mm.) by efficient diffusion pumps. A fine beam of electrons is accelerated through a measured potential of

the order of 50,000 volts and then crosses a horizontal beam of molecules of the material under examination. The molecular beam is produced by allowing the gas or vapour to enter the highly evacuated space through collimating orifices, and is condensed out when it impinges on a surface cooled in liquid air situated directly opposite the point of entry of the beam. The electron beam which has crossed the molecular beam falls on a photographic plate. The efficiency of scattering of electrons by matter is much greater than that of X-ray scattering. The exposure time is of the order of one second, which is much shorter than that needed in studying the diffraction of X-rays by gaseous molecules. The intensity distribution in the photographic plate after the exposure is measured by standard techniques.

The range of substances examined by this technique may be judged by a recent publication of Allen and Sutton,¹ in which results for five hundred compounds are collected. Roughly two hundred of these are simple volatile inorganic substances, for most of which the chief interatomic distances and valency angles have been determined. The results tabulated below are typical.

Table 1

<i>Molecule</i>	<i>Configuration</i>	<i>Bond distances (Å)</i>
NaCl		Na—Cl, 2.51
HgCl ₂	Linear	Hg—Cl, 2.27
HgBr ₂	Linear	Hg—Br, 2.44
HgI ₂	Linear	Hg—I, 2.61
B ₃ N ₃ H ₆	Reg. hexagon	B—N, 1.44
BCl ₃	Planar	C—Cl, 1.73 ; \angle Cl—B—Cl, 120°
SiCl ₄	Tetrahedral	Si—Cl, 2.02
GeCl ₄	Tetrahedral	Ge—Cl, 2.08
TiCl ₄	Tetrahedral	Ti—Cl, 2.18
P ₄	Tetrahedral	P—P, 2.21
PF ₃	Pyramidal	P—F, 1.52 ; \angle F—P—F, 104°
OF ₂	Non-linear	O—F, 1.41 ; \angle O—F—O, 100°
OCl ₂	Non-linear	O—Cl, 1.68 ; \angle Cl—O—Cl, 115°
SO ₂	Non-linear	S—O, 1.43 ; \angle O—S—O, 120°
CS ₂	Linear	C—S, 1.54
SF ₆	Octohedral	S—F, 1.58
Ni(CO) ₄	Tetrahedral	N—C, 1.82 ; C—O, 1.15

The estimated uncertainty in bond lengths determined by the electron diffraction method is usually of the order of ± 0.05 Å. The diffraction of the electron beam is a function of the atomic number

¹ *Acta Crystallographica*, 1950, 3, 46.

of the atom and is a nuclear phenomenon. It follows that hydrogen atoms in a molecule make little contribution to the diffraction, and it is not possible as a rule to determine the positions of hydrogen atoms by this method. The phenomenon of neutron diffraction, which gives results similar to those by the electron diffraction method, offers a much greater prospect of determining the position of light atoms in molecules when the experimental methods have been fully developed.

The lengths of bonds as determined by electron diffraction, and to a small extent by other methods, have been of great assistance in the development of theories of valency, especially in connexion with the idea of resonance. The limitations of this approach are, however, becoming increasingly apparent.² From the large number of structural determinations available it is now realized that there are numerous deviations from the principle that the length of a bond is given by the sum of the covalent radii of the atoms concerned. Such deviations may be discussed in terms of partial ionic character in the bond and also in terms of multiple bonds. Bonds of integral orders are probably much less common than was formerly supposed; only in organic chemistry, however (*e.g.* for carbon-carbon bonds), are sufficient data for detailed discussion available.

Spectroscopic Evidence of Molecular Structure.—The information about molecular structure obtained by electron diffraction experiments may be to some extent confirmed and augmented by spectroscopic studies. These include the examination of the electronic spectra of molecules, which gives a picture of the quantized electronic, vibrational and rotational energy, and also studies of the infra-red and Raman spectra, which afford a means of studying the vibrational and rotational energies of molecules. It is not proposed here to discuss either the theoretical background of this extensive field or its practical aspects, but rather to indicate by a few selected examples the type of information which may be derived.

Considering first the case of diatomic molecules, the internal energy is of three types, electronic, vibrational and rotational, all of which are quantized. A change in the electronic energy of the molecule alone, if this were possible, would result in the emission or absorption of a single frequency corresponding to the energy difference between the initial and the final states. In such a change, however, there are always simultaneous changes in the vibrational and rotational energies. These result in the emission or absorption of a series of bands, which represent the changes in vibrational energy and have fine structure due to changes in

² For a critical review, see Wells, *J.C.S.*, 1949, 55.

rotational energy. The information to be gained from an analysis of the electronic spectrum comprises, therefore, not only the difference in energy between the two states of the molecule, but also a picture of its vibrational and rotational characteristics.

It is possible, also, to study changes in the vibrational and rotational energy without a change in the electronic energy. The energy changes are smaller in this case and the resulting band spectrum normally lies in the infra-red. It is usually studied by means of absorption rather than emission measurements. The study of microwave (far infra-red) spectra makes it possible to investigate rotational changes alone; very accurate structural parameters may be obtained in this way. The most significant quantities which can be derived from this approach to the structure of diatomic molecules are their dissociation energies, internuclear distances and vibration frequencies. Dissociation energies are derivable because dissociation represents the limit to which vibrational excitation of the molecule can be extended. The dissociation energies are most commonly identified as those corresponding to the point of convergence of a series of vibrational bands in an absorption spectrum, at which, with increasing energy, a continuous spectrum is observed. The internuclear distance of a diatomic molecule is derived from those features of its spectrum which are concerned with molecular rotation. First the moment of inertia of the molecule is derived and from this, knowing the nuclear masses, the interatomic distance can be obtained.

Diatomic Molecules.—By way of illustration of the data obtained for diatomic molecules, the internuclear distances (d , in Å.) for chlorine, bromine and iodine derived from spectroscopic measurements and electron diffraction may be compared:

Table 2

<i>Molecule</i>	<i>d. from spectroscopy</i>	<i>d. from electron diffraction</i>
Cl ₂	1.99	2.01
Br ₂	2.28	2.28
I ₂	2.67	2.65

Gaydon³ has tabulated the dissociation energies of over 200 diatomic molecules derived spectroscopically. Their dissociation energies, representing the energy difference between the lowest vibrational level and that for infinite separation of the nuclei, are most readily

³ Gaydon, *Dissociation Energies and Spectra of Diatomic Molecules*, London, 1947.

obtained spectroscopically. The molecules for which spectroscopic values have been obtained include a number for which thermochemical data are available and the agreement is usually good. It may be noted also in passing that a considerable number of molecules may be produced and studied by spectroscopic techniques which have no stable chemical existence. These include molecules such as AlCl , BF , BiH , CH , MgCl , OH and PO which are known to be, or might well be, intermediates in chemical reactions. As an example of data for heteropolar diatomic molecules, the moments of inertia (I) and interatomic distances (d) of the halogen hydrides, derived from a study of the far infra-red adsorption spectra, may be quoted.

Table 3

Gas	$I \times 10^{40} \text{ (g. cm.}^2\text{)}$	$d \text{ in } \text{\AA}$
HF	1.346	0.923
HCl^{35}	2.649	1.281
HCl^{37}	2.653	1.281
HBr	3.311	1.420
HI	4.308	1.617

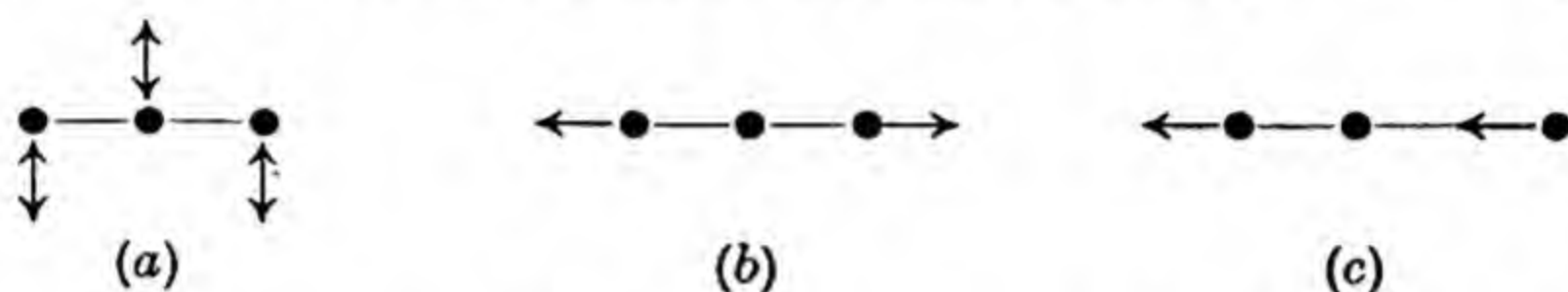
These values illustrate the gradual increase in interatomic distance and moment of inertia with increase in atomic weight of the halogen. In the case of HCl^{35} and HCl^{37} the difference in moment of inertia and the equality of interatomic distances may also be noted. This 'isotope effect' has been observed in the band spectra of many molecules, each isotope registering its own spectrum in so far as the vibrational and rotational characteristics of the molecule are concerned. It was in this way that the existence of the oxygen isotopes O^{17} and O^{18} was first recognized and the difference between the physical and the chemical atomic weight standard was established.

Polyatomic Molecules.—The majority of molecules known to the chemist contain more than two atoms and for these the problems of studying the electronic spectrum are complex and, as a rule, insoluble. Fortunately the vibrational and rotational characteristics may be elucidated by studying the infra-red absorption spectrum and the Raman spectrum. The nature of the latter is best explained by taking the simple case of a gas or liquid irradiated with light of a single frequency. If the spectrum of the light emerging from the medium is examined it is found to show not only a line corresponding to the incident frequency, but also certain other lines, of very low intensity. The intensity of the latter, relative to that line due to the incident light, may be greatly increased

by photographing only the light emitted at right angles to the direction in which the incident beam passes through the medium.

The energy differences corresponding to differences in frequency of the incident light and that of the new weak lines in the spectrum (the Raman lines) correspond to quanta which are, so to speak, abstracted from the incident light and used to excite the characteristic frequencies of the molecules in the medium. There are certain limitations to the frequencies which can be so excited and observed in the Raman spectrum⁴ but infra-red and Raman spectra taken together give a fairly complete picture of the modes of vibration and rotation of a wide range of species.

As an example of the characteristic frequencies of a relatively simple molecule, the possible modes of vibration of a linear triatomic molecule such as carbon dioxide are shown below:—



Of these (a) represents a bending frequency, while (b) and (c) are respectively symmetrical and unsymmetrical vibration frequencies in the line of the molecule. As a further illustration of the significance of the characteristic modes of vibration the case of diborane may be mentioned (*see* p. 278). The problem which arises is to determine whether the molecule is structurally like ethane or like ethylene. These two molecular types have considerable differences in their possible modes of vibration, largely because the double bond in ethylene renders free rotation about the C—C bond impossible. Complete analysis of the Raman and infra-red spectrum of diborane gives a picture which is in accordance with the ethylene molecule.

The analysis of the infra-red spectrum of simple polyatomic molecules enables moments of inertia and interatomic distances to be calculated. Results obtained in this way are shown opposite.

For complicated molecules it is not possible to analyse completely the vibrational and rotational spectra, but the infra-red and Raman spectra give important information bearing on the presence of particular bonds in a molecule. In the idealized case a particular bond (*e.g.* C—H, C—C, O—H) will have a characteristic vibrational frequency. Actually the value is modified—often quite considerably—by neighbouring groups. In spite of this complication, how-

⁴ See Syrkin and Dyatkina, *Structure of Molecules and the Chemical Bond* London, 1950.

ever, vibrational frequencies have played a very important part in structural determinations, particularly for organic molecules. The

Table 4

<i>Molecule</i>	<i>Moment of inertia g. cm.² × 10⁴⁰</i>	<i>Interatomic distances (Å)</i>
CO ₂	70.2	C—O = 1.16
C ₂ H ₂	23.5	C—C = 1.20
		C—H = 1.06
CH ₄	5.47	C—H = 1.11
		H—H = 1.81
NH ₃	2.8	N—H = 1.02
	4.4	H—H = 1.64
H ₂ O	0.995	O—H = 1.01
	1.908	H—H = 1.91
	2.980	
H ₂ S	2.68	S—H = 1.35
	3.08	H—H = 2.24
	5.85	

table below shows the approximate frequency range of the vibrational frequencies associated with a number of common bonds in carbon compounds.

Table 5

<i>Bond</i>	<i>Frequency (cm.⁻¹)</i>	<i>Bond</i>	<i>Frequency (cm.⁻¹)</i>
C—H	3500–3700	C=O	1550–1850
O—H	3500–3700	C≡O	2160
C—C	800–860	C=N	1650
C=C	1600–1650	C≡N	2150
C—C	2100–2450		

The usefulness of this method in diagnostic work has been greatly increased by the development of infra-red spectrometers with a high resolution.

Another characteristic of molecules which can, in theory at least, be derived from the study of the vibrational frequencies of bonds is the so-called force constant, which measures the resistance of a bond to stretching. As a first approximation the axial vibration of two atoms along the bond axis may be treated as simple harmonic, and the restoring force per unit displacement may be directly calculated from the vibration frequency. There are a number of factors which complicate this picture,⁶ but the following figures, based on

⁶ See Linnett, *Quart. Rev. Chem. Soc.*, 1947, 1, 73.

the above simplified approach, serve to illustrate how the method brings out the difference between bonds of various types between the same two atoms.

Table 6

<i>Bond</i>	<i>Force constant</i>	<i>Bond</i>	<i>Force constant</i>
C—C	4.6×10^{-5}	C—O	4.9×10^{-5}
C=C	9.5×10^{-5}	C=O	12.3×10^{-5}
C≡C	15.8×10^{-5}	C≡O	18.6×10^{-5}

The Dipole Moments of Some Inorganic Compounds.—An electrical dipole is best represented as two equal electrical charges of opposite sign, $+e$ and $-e$, separated by a distance d . The dipole moment is then equal to the product $d \times e$. It is important in the first place to consider the way in which the idea of dipole moments is of interest to chemists. Any two atoms, if joined by valency forces, may constitute a dipole. In the simple case of a molecule of sodium chloride in the vapour state, for example, the sodium and chlorine atoms have opposite charges and are separated by a characteristic internuclear distance, so that the molecule must have a definite dipole moment. This will be true for any ionic molecule, but it may also be true for a purely covalent molecule. In gaseous hydrogen chloride, which for purpose of the argument may be taken as covalent, the two electrons which make up the bond will be unequally shared. The hydrogen atom has, in effect, a fractional positive charge and the chlorine a negative, so that the molecule has a dipole moment equal to the electronic charge multiplied by a distance, which represents the effective charge separation and is less than the true internuclear distance. Only when two like atoms are joined by a covalent bond will the bonding electrons be equally shared. In this case, as has been amply verified from molecules such as H_2 , O_2 , N_2 , Cl_2 , etc., the dipole moment is zero.

The actual methods by which the permanent dipole moments of molecules are determined will not be discussed here. It may be remarked in passing, however, that the quantity is not one which can be measured directly. This is because polarity is induced in any molecule when it is placed in an electric field, irrespective of whether permanent dipoles are present in the molecule or not. The applications of dipole measurements in the study of molecular structure may be classified under the following two headings:

- (1) The determination of the shapes of molecules.
- (2) The determination of bond types.

In discussing the use of dipole moments to determine the shapes of molecules, the dipole is treated as a vector. Carbon dioxide, for

example, is found to have zero dipole moment, even though it is certain that each of the C—O bonds has a permanent moment. This must mean that in the molecule the two bond moments neutralize one another, which can happen only if the molecule is linear with the carbon atom at the centre. A few similar instances in which the dipole moment serves to distinguish between symmetrical linear structures with zero moment and non-linear molecules with finite resultant moments are given below:—

Table 7

<i>Molecule</i>	$\mu \times 10^{18}$	<i>Molecule</i>	$\mu \times 10^{18}$
CO ₂	0	H ₂ O	1.71–1.97
HgCl ₂	0	SO ₂	1.60–1.76
HgBr ₂	0	H ₂ S	0.93–1.10
HgI ₂	0	NO ₂	0.4–0.1

The unit used is the Debye (D), which equals 10^{-18} e.s.u. The convenience of this unit will be recognized when it is remembered that the electronic charge is 4.8×10^{-10} e.s.u. and the internuclear distances in molecules are of the order of 10^{-8} cm. The range in the values quoted reflects the variation in the measurements of different observers using different methods. The most accurate experimental method involves the measurement of the dielectric constant of the vapour at a series of temperatures: other less accurate, but more convenient, methods involve uncertain corrections.

The above argument for linear molecules may be applied to other configurations. The data given below for other tetra-atomic molecules, for example, show a resultant moment which rules out the existence of a symmetrical planar structure. Thus in ammonia the nitrogen atom is at the apex of a pyramid and the three hydrogen atoms are at the corners of the base. The components of the dipole vectors at right angles to the plane of the base do not cancel. The other molecules have similar pyramidal configurations.

Table 8

<i>Molecule</i>	$\mu \times 10^{18}$	<i>Molecule</i>	$\mu \times 10^{18}$
NH ₃	1.48	AsF ₃	2.65
PH ₃	0.55	AsCl ₃	2.06
AsH ₃	0.16	AsBr ₃	1.60
PCl ₃	0.85	AsI ₃	0.96
PBr ₃	0.61		

Molecules of the type AB_4 (e.g. CCl_4 , $SiCl_4$, $SnCl_4$, $TiCl_4$, SiH_4 , SiF_4 and $Ni(CO)_4$) are found in most cases to have zero resultant dipole moments, and are then believed to have tetrahedral structures, resulting in complete cancellation of the constituent dipoles. A great deal of attention has been devoted to the more complex problem of the dipole moments of larger organic molecules, for the determination both of valency angles and of bond types, but the discussion of this field lies outside the scope of this book.

The general conclusions as to the configurations of the molecules discussed are in agreement with the results obtained by methods such as electron diffraction. Quite apart from problems of configuration, dipole moment measurements also give important information on bond types. That this should be possible in principle follows the definition of the dipole moment as the product of the electronic charge and a distance, which is equal to the internuclear distance only in the case of a purely electrovalent bond. If a molecule of HCl , for example, were purely electrovalent, the dipole moment would be the product of the electronic charge (4.8×10^{-10} e.s.u.) and the internuclear distance (1.28×10^{-8} cm.), as determined from the infra-red spectrum. This gives a value of 6.14×10^{-18} (or 6.14 D). The observed moment is 1.04 D. If the actual structure of the molecule be regarded as a combination of the ionic structure and the covalent structure with zero dipole moment (which in fact is not correct), the ionic character of the bond may be expressed by the ratio $1.04/6.14$, or as 17 per cent electrovalent. By this approximate method the following estimates of the ionic character of bonds have been made :⁶

Table 9

Bond	Bond moment (D)	Ionic character %	Bond	Bond moment (D)	Ionic character %
H—F . . .	1.91	43	Pb—Cl . . .	4.1	34
H—Cl . . .	1.04	17	Pb—Br . . .	4.0	31
H—Br . . .	0.78	11	Pb—I . . .	3.4	25
H—I . . .	0.38	5	Na—I . . .	4.9	35
Ge—Cl . . .	2.0	19	K—Cl . . .	6.3	47
Ge—Br . . .	2.2	19	K—I . . .	6.3	44
Sn—Cl . . .	3.1	27			

Magnetic Susceptibility and Chemical Constitution.—Magnetic measurements are of importance in solving problems of

⁶ These data are quoted from an article by Smyth in *Frontiers of Chemistry*, vol. 5 (Interscience Publishers, New York, 1948).

molecular structure and bond type because they afford a means of detecting the presence of singly-occupied electronic orbits. Before proceeding to a review of some of the applications of such measurements, however, it is necessary to outline the relationships between magnetic properties and electronic structure.

When a substance is placed in a magnetic field of strength H gauss, polarity is induced in the atoms or molecules present. If the intensity of this induced magnetization be I , the total magnetic flux is given by $B = H + 4\pi I$. The ratio $B/H (= \mu)$ is called the magnetic permeability of the medium and the quantity $I/H (= \kappa)$ its volume susceptibility. Dividing the expression for the magnetic flux throughout by H , the equation $\mu = 1 + 4\pi\kappa$ is obtained. In a vacuum $B = H$: there is no induced magnetization and the susceptibility $\kappa = 0$. In any other medium κ is either positive, when the medium is said to be paramagnetic, or negative, when it is diamagnetic. For the discussion of chemical problems, the susceptibility per gram molecule is of greater value than the susceptibility per cubic centimetre: this is given by $\chi_M = \frac{M\kappa}{\rho}$,

where ρ is the density.

A paramagnetic substance increases the flux due to the applied field alone, whereas a diamagnetic substance diminishes it. It is convenient to consider first of all the reasons for the reduction in the case of diamagnetic substances. Diamagnetism arises from the interaction of the applied magnetic field with the filled electronic orbits of the atoms of the medium. It is not necessary here to discuss the detailed physical picture: the result is that the direction of the magnetic field due to the induced polarity in each atom in the medium is opposed to that of the applied field and the magnetic flux is thereby reduced. The magnitude of diamagnetic effects is small. It is independent of temperature because the induced polarity is the same whatever the orientation of the atoms or molecules with respect to the applied field.

The atoms or molecules of a paramagnetic substance on the other hand have permanent magnetic moments and tend, therefore, to become orientated in an applied field. This orientation is disturbed by increase in temperature and the phenomenon of paramagnetism is accordingly temperature dependent. It must be remembered, however, that even in a paramagnetic substance the induced polarity which has been mentioned as characterizing diamagnetic substances will again be operative. Its magnitude however is small compared with the permanent paramagnetic moment. The two effects are opposed and the nett result is always that the orientated permanent moments in the medium augment the flux due to the applied field,

leading to a positive value for the susceptibility. For a very restricted group of substances another phenomenon, known as ferromagnetism, occurs, leading to positive values of the susceptibility which are very large compared with those for paramagnetic substances. Ferromagnetism is generally considered as arising from orientation of whole domains each of which behaves as a magnet, and is thus not directly related to the topic under discussion. Paramagnetic substances at low temperatures do, however, show a behaviour which corresponds to ferromagnetism. The temperature dependence of paramagnetic susceptibility is expressed by the empirical Curie law $\chi = \frac{C}{T}$, where C is a constant, or more exactly

by the Curie-Weiss law $\chi = \frac{C}{T - \Delta}$. The term Δ may be interpreted as representing the mutual interaction of the molecular magnets. It has the dimensions of temperature and may be positive or negative. When it is positive there will be a certain value of T at which the susceptibility becomes very large. This is known as the Curie point and may be interpreted as the temperature at which the molecular orientation is maintained against the thermal agitation.

It is possible to proceed a stage further in the interpretation of paramagnetism. An electron circulating in its orbit, or spinning about its axis, amounts to a circular electric current, and as such is equivalent to a magnet with a moment $\mu_e = \frac{he}{4\pi mc}$. In a doubly occupied orbit, however, this magnetic moment is compensated by the equal and opposite moment of the second electron, which must on the Pauli principle have the opposite angular momentum. We may thus identify the elementary magnet of paramagnetic atoms, ions and molecules with the magnetic effect of unpaired electrons. It follows that only those atoms, ions or molecules containing incomplete electron shells with unpaired electrons should be paramagnetic, and that the magnetic moment of paramagnetic ions should be expressible as a multiple of the unit μ_e above. This latter unit, known as the Bohr magneton, has the value 5564 gauss-cm. for one gram molecule.

A number of theoretical expressions have been advanced to represent quantitatively the magnetic moment of paramagnetic ions in terms of their atomic structures. Thus, for ions of the transition metals, the expression μ_A (the magnetic moment in Bohr magnetons) $= \sqrt{4S(S + 1) + L(L + 1)}$, where S is the resultant spin (*i.e.* $2S$ = number of unpaired electrons) and L is the resultant

angular momentum, should be approximately true. In this case the contribution of the orbital angular momentum is, however, negligible. This is because, in the transition metal ions, the incomplete shells are also the outermost shells. The interaction of other ions in solution or in crystals is sufficient to cancel out the whole or the greater part of the orbital magnetic moments. As a result the magnetic moments are approximately represented by considering the electron spin only, *i.e.* $\mu = 2\sqrt{S(S+1)}$. The variation of magnetic moment as calculated for spin only as the 3*d* shell is progressively filled is shown in Fig. 25, which indicates also the magnetic moment found experimentally for typical compounds of the transition elements due to the presence of the metal ion. The

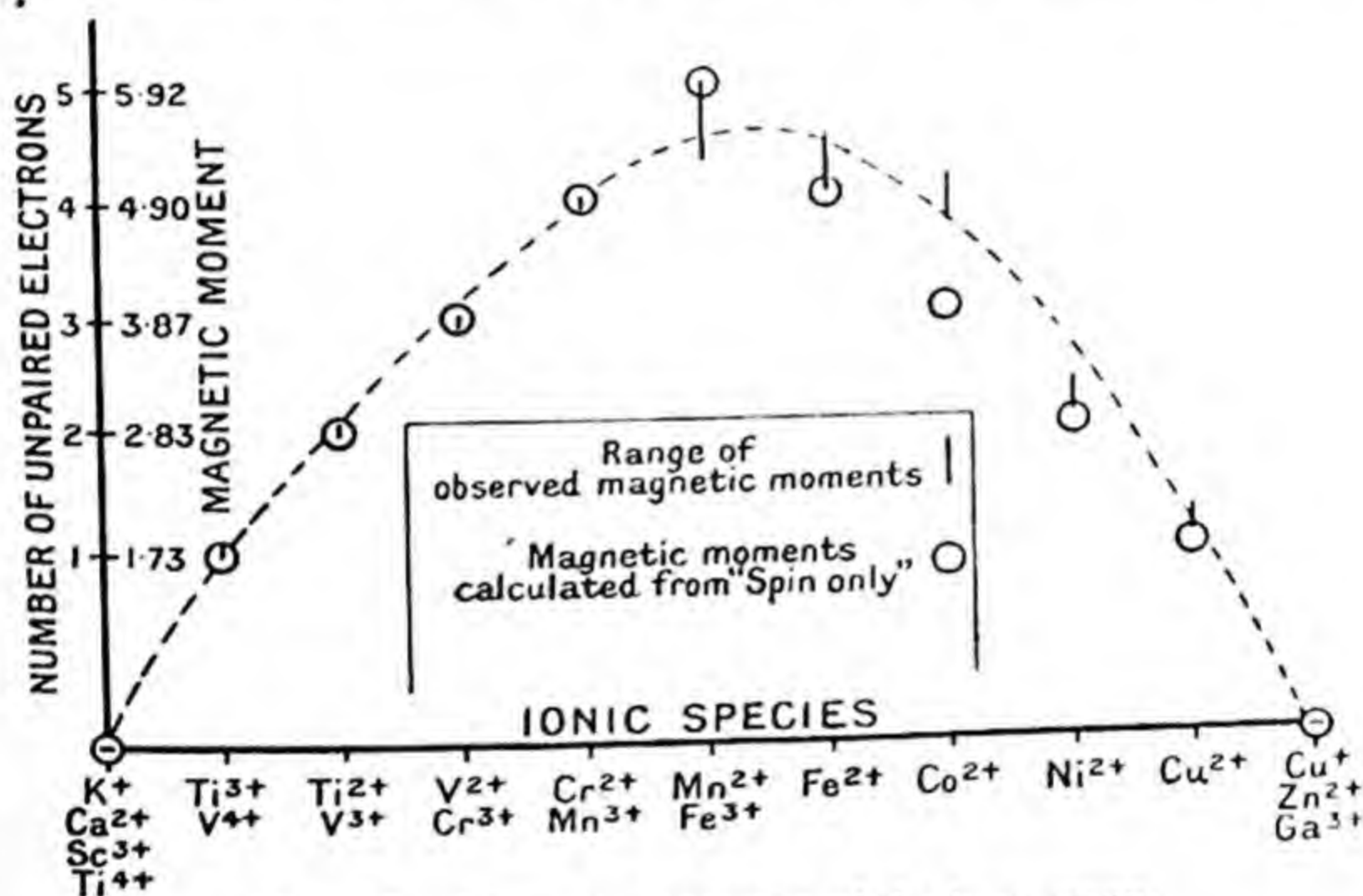


FIG. 25.—Magnetic moments of the iron group.

compounds considered are simple salts and oxides—such as CoCl_2 , $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ and Cr_2O_3 : in the complex salts of these elements the magnetic evidence shows that far-reaching rearrangements of electronic levels take place, so that compounds such as hexamine cobaltic chloride, $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$, and potassium ferrocyanide, $\text{K}_4\text{Fe}(\text{CN})_6$, are actually diamagnetic. The consideration of this striking phenomenon is deferred to a later section (p. 167) in which the constitution of the complex salts is discussed.

In the ions of the rare earth elements the magnetism arises from the filling of the 4*f* shell. As this is screened by the 5*s* and 5*p* shells, the magnetic moment is not given by consideration of the resultant spin only. It is necessary to take count also of the orbital angular momentum. The experimental values and those calculated by Van

Vleck are reproduced in Fig. 26. The magnetic moments of ions of the actinides (*see* p. 403) are less well known but they appear to parallel those of the rare earth ions with corresponding electronic configurations.

The use of magnetic measurements to determine the number of unpaired electrons is subject to certain limitations, as has already been indicated, but is, nevertheless, useful in a number of cases. A very simple illustration is afforded by magnetic measurements on copper salts. Cuprous salts are diamagnetic, which confirms that copper has the configuration $d^{10}s$ and uses the single s electron in the formation of cuprous compounds. In cupric salts, which are paramagnetic, an additional electron is used in bond formation, leaving $9d$ electrons in the ion, one of which must be unpaired.

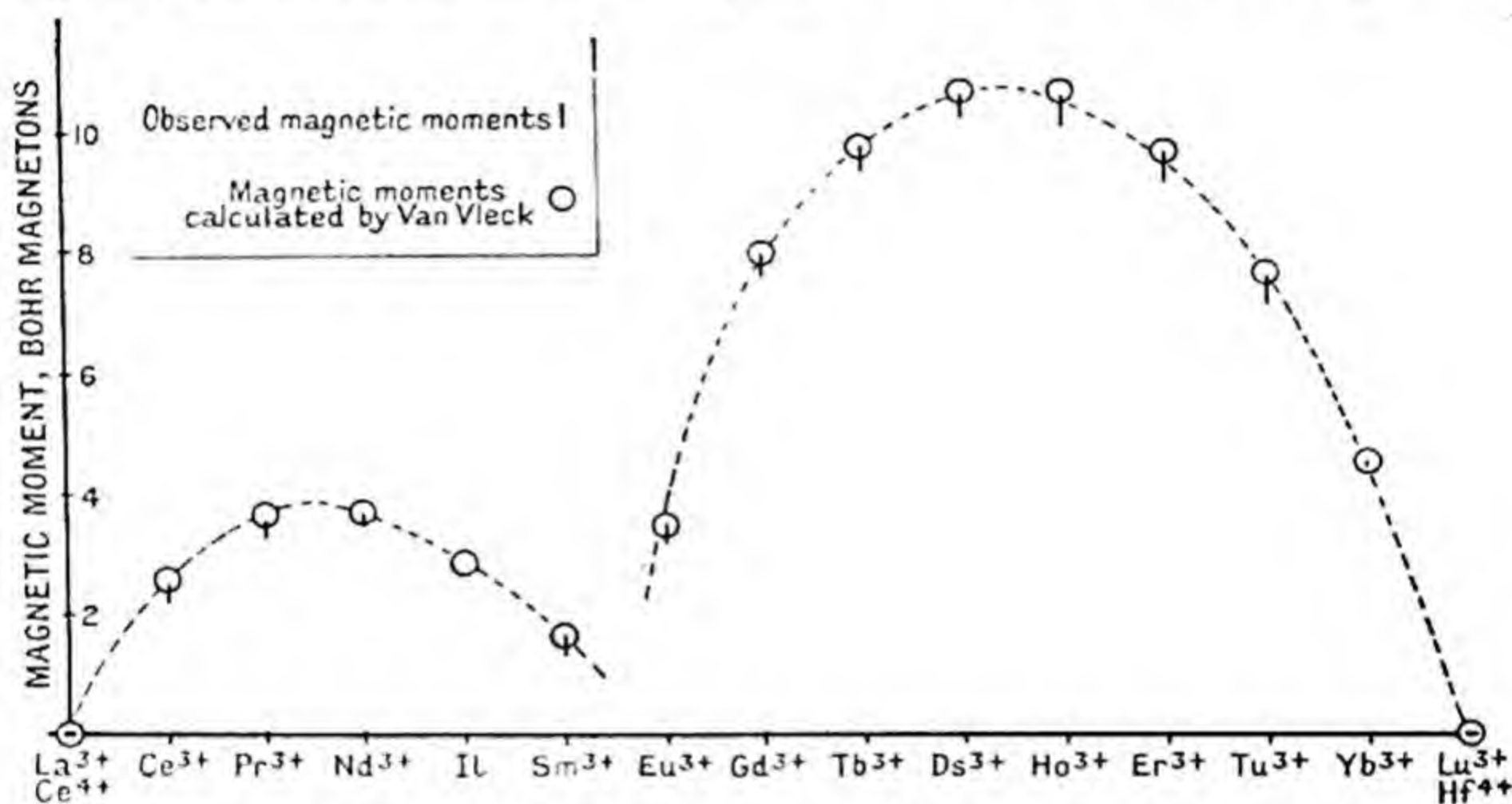


FIG. 26.—Magnetic moments of rare earth ions.

Reference is made elsewhere to so-called 'odd electron molecules', of which nitric oxide is an excellent example. In this case there are in the molecule fifteen electrons, so that it is impossible for all to be paired. In accordance with this view, nitric oxide is paramagnetic. The molecule NO_2 has also an odd number of electrons and is paramagnetic, whereas the dimer, N_2O_4 , is, as would be expected, diamagnetic. Chlorine dioxide is another example of a molecule with an odd number of electrons which is paramagnetic. The molecular susceptibilities of these paramagnetic molecules are about 1400×10^{-6} e.m.u., the theoretical value for a single electron with an uncoupled spin being 1300×10^{-6} e.m.u.

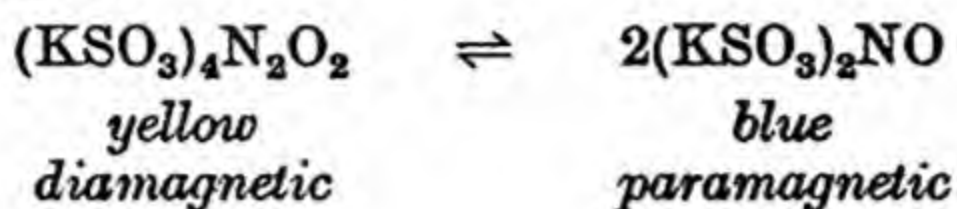
This approach may occasionally be of value in deciding between the single and double formula for a compound. Silver and sodium

Table 10
Summarizing Table

<i>Magnetic property</i>	<i>Variation with temperature</i>	<i>Origin of effect</i>	<i>Effect shown by</i>	<i>Examples</i>	<i>Magnitude of effect</i>
Ferromagnetism	Passes over into paramagnetism at the Curie point	Parallel orientation of molecular magnets over microscopic regions of the solid, e.g. over each unit crystal-lite	Iron group metals, some of their compounds, Heusler alloys, etc.	Fe	Very large, $\chi \rightarrow \infty$
Ionic paramagnetism	$\chi \propto \frac{1}{T}$ or $\frac{1}{T - \Delta}$	Resultant spin or orbital angular momentum of incomplete electronic shells	Ions of the transition and rare earth metals	Cu^{2+} , Co^{2+} , Nd^{3+}	Large $\chi_A = 10^{-3} - 10^{-2}$
Metallic paramagnetism	Independent of T	Uncompensated spin of the metallic conduction electrons	Alkali metals, Cu, Ag, etc. Some interstitial carbides, nitrides, etc.	Na, Ag, TiN	Small $\chi_M \sim 10^{-5}$
Diamagnetism	Independent of T	Interaction of magnetic field with closed electronic shells	Rare gas-like ions. Complex ions of the transition metals. ⁷	Na^+ , Br^- , Cu^+ $[\text{Co}(\text{NH}_3)_6]^{3+}$ $[\text{Fe}(\text{CN}_6)]^{4-}$	Small $\chi_A \sim 10^{-5} - 10^{-6}$
Residual paramagnetism	Independent of T	Uncompensated paramagnetism of complex ions	Polyatomic ions (especially oxyacid ions) of transition elements	MnO_4^- MoO_4^{2-}	Small $\chi_M \sim 10^{-5}$

⁷ These may show a residual paramagnetism where accurate measurements are available.

hypophosphates, for example, have the empirical formulæ NaHPO_3 and Ag_2PO_3 , but if these were the true molecular formulæ the compounds would be paramagnetic. In fact, both salts are diamagnetic, so that, in accordance with other evidence, the double formulæ $\text{Na}_2\text{H}_2\text{P}_2\text{O}_6$ and $\text{Ag}_4\text{P}_2\text{O}_6$ must be adopted. In the same way Fremy's salt, a yellow compound of the formula $(\text{KSO}_3)_2\text{NO}$, is diamagnetic in the solid state, although on the single formula it should be an odd electron molecule and paramagnetic. This shows that in the solid the formula must be doubled. Its solution, however, is deep blue in colour and paramagnetic, indicating that dissociation occurs:



CHAPTER VI

CO-ORDINATION COMPOUNDS AND INORGANIC STEREOCHEMISTRY

In the chemistry of the metallic elements, few generalizations have proved so fruitful as those based upon the study of molecular compounds, *i.e.* of those compounds formed by the union in stoichiometric ratio of otherwise saturated molecules, themselves capable of independent existence. As examples of such molecular compounds may be cited the highly characteristic ammoniates of trivalent cobalt—*e.g.* $\text{Co}(\text{NH}_3)_6\text{Cl}_3$; the numerous complex cyanides—*e.g.* $\text{K}_4\text{Fe}(\text{CN})_6$ or $4\text{KCN}.\text{Fe}(\text{CN})_2$; the alums—*e.g.* $\text{NH}_4\text{Al}(\text{SO}_4)_2.12\text{H}_2\text{O}$ —and the many other double salts.

It is not necessary to consider the various older views upon the constitution of such molecular compounds, such as those associated with the names of Blomstrand and Jörgensen, since the co-ordination theory of Werner has proved far-reaching in its scope, and has been fully substantiated by both chemical and physical evidence. According to Werner, without invoking any special theory of valency, neutral molecules or oppositely charged ions are grouped or *co-ordinated* around a central ion in the 'first sphere of attraction', or *co-ordination sphere*. The number of groups which may be so arranged about the central ion is the *co-ordination number*, and is a characteristic property of that ion; in general, the co-ordination number can assume only those values (2, 3, 4, 6, 8) which allow of spatially symmetrical arrangements, the values 6 and 4 being most usual. In this way, in hexammine cobaltic chloride, six ammonia molecules are co-ordinated about the cobaltic ion, forming a new *complex ion* $[\text{Co}(\text{NH}_3)_6]^{3+}$; the chlorine is bound in the 'second sphere of attraction', *i.e.*, in terms of modern conceptions, exists as an independent anion. The co-ordination of negative ions is exemplified by the ferrocyanide anion $[\text{Fe}(\text{CN})_6]^{4-}$, in which six CN^- ions are co-ordinated about a central ferrous ion, forming thereby a complex anion with a nett negative charge of four units.

A great many molecular compounds or double compounds fall naturally within the scope of this mode of formulation, which implies, as will be discussed below, definite chemical combination between the co-ordinated groups and the central atom. In order

to delimit its applicability, and to avoid artificiality in its application, it is desirable to define more strictly the conception of a molecular compound. The criterion of this may well be the persistence of the molecular compound, as a co-ordinated complex, in solution. The X-ray study of crystals has shown that the crystal lattice may in certain cases contain units which are not combined in a chemical sense, but which, by crystallizing together in stoicheiometric ratio, form a new lattice with, presumably, a more compact structure and lower lattice energy than would be formed by either constituent alone. On the dissolution of the crystal, the units part company, and the stoicheiometric 'compound' ceases to exist. Such combinations, forming as they do a unique and stoicheiometric crystalline phase, may be termed *lattice compounds*, and to this class belong many compounds which can be accounted for only with difficulty on the Werner theory, or which would involve unusual or unsymmetrical co-ordination numbers. Thus caesium chloride forms with cobalt chloride a double salt of the formula Cs_3CoCl_5 , in which cobalt apparently has the co-ordination number 5, which, apart from covalent compounds (PCl_5 , IF_5) and the isolated case of iron pentacarbonyl, $\text{Fe}(\text{CO})_5$, is unknown. The crystal structure of Cs_3CoCl_5 shows, however,¹ that in the lattice there exist independently both CoCl_4^{2-} and Cl^- anions; in solution there is no evidence for the persistence of a CoCl_5^{3-} anion. This compound should therefore be regarded as a lattice compound of $\text{Cs}_2\text{CoCl}_4 + \text{CsCl}$, existing only in the solid phase. Nevertheless, it does appear from the crystal structure of $(\text{NH}_4)_3[\text{ZrF}_7]$ ² and $\text{K}_2[\text{TaF}_7]$ ³ that complex anions involving the co-ordination number seven are capable of existence. The alums and numerous other double salts belong, however, to the class of lattice compounds. The alums, from their crystal structure, are known to be built up of alkali metal, $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$, and SO_4^{2-} ions, the last two of which may well be cemented together in the solid phase by the additional water molecules, as is discussed in a later section. In solution, however, each ionic species is independent, the whole forming only a lattice compound. A great number of double salts belong to this type, and also many addition compounds involving neutral molecules—e.g. the water-rich hydrates of many alkali metal salts, and also many organic molecular compounds.

The distinction between the lattice compounds and the true molecular complexes is rather well illustrated by the contrast in

¹ Powell and Wells, *J.C.S.*, 1935, 359.

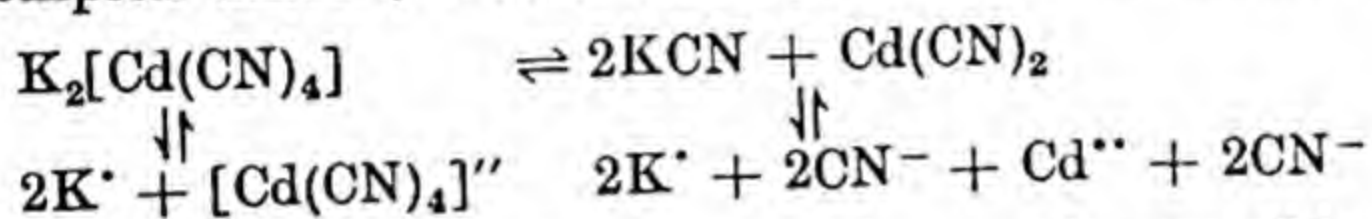
² G. C. Hampson and L. Pauling, *J.A.C.S.*, 1938, 60, 2702.

³ J. L. Hoard, *J.A.C.S.*, 1939, 61, 1252.

properties between the brown rhodium alum $\text{CsRh}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ and the red double sulphate $\text{Cs}[\text{Rh}(\text{SO}_4)_2] \cdot 4\text{H}_2\text{O}$, which is formed when solutions of the alum are evaporated. That it contains a true complex anion $[\text{Rh}(\text{SO}_4)_2]^-$ is shown in that its solution gives no immediate precipitate with barium chloride, whereas the alum shows all the reactions of the sulphate ion.

Of the true molecular compounds, which exist also in solution, two limiting types may plainly be recognized:

(a) Those compounds, such as the ammoniates of metallic salts—e.g. $\text{CoCl}_2 \cdot 6\text{NH}_3$ —which are reversibly dissociated into their components either in the solid phase or in solution, and in which therefore the linking of the constituents is but loose. These are termed by Biltz ⁴ *normal complexes*. To them may be ranked also many complex anions, which undergo similar dissociation: e.g.



(b) Compounds which afford no evidence of reversible dissociation, in which the co-ordinate linkage is indistinguishable in strength and directional properties from a normal covalency. Such complexes, termed by Biltz *penetration complexes*,⁵ are exemplified by the hexammine cobaltic cation $[\text{Co}(\text{NH}_3)_6]^{3+}$ and the ferrocyanide anion $[\text{Fe}(\text{CN})_6]^{4-}$. It is plain, however, that these represent limiting types rather than clear divisions. Some evidence as to the relative stability and the step-wise dissociation of some typical penetration complexes is mentioned later in this chapter.

The Basis of the Werner Theory.—It is well to consider in some detail the experimental evidence, relating principally to the cobaltammines, upon which the co-ordination theory is based. In the presence of ammonia and ammonium salts, cobaltous salts are readily oxidized by atmospheric oxygen, giving, according to conditions, mixtures of a number of cobaltic salts containing ammonia. Amongst these is an orange-yellow salt, known as luteocobaltic chloride, having the composition $\text{CoCl}_3 \cdot 6\text{NH}_3$. With silver nitrate, this salt precipitates all its chlorine, leaving in solution a nitrate of the composition $\text{Co}(\text{NO}_3)_3 \cdot 6\text{NH}_3$. On treating the solid salt with concentrated sulphuric acid, hydrochloric acid is displaced, but no ammonia is removed, and there is formed a corresponding sulphate, $\text{Co}_2(\text{SO}_4)_3 \cdot 12\text{NH}_3$; similarly, concentrated hydrochloric acid at 100° effects no decomposition. Hot caustic

⁴ W. Biltz, *Z. anorg. Chem.*, 1927, 164, 345.

⁵ The term penetration complex is used to imply the abnormally small molecular volume occupied by ammonia in such compounds. See p. 166.

alkalis decompose the compound with formation of Co_2O_3 , but moist silver oxide yields a solution of a strong, very soluble base, which absorbs carbon dioxide from the air, and re-forms salts of the general formula $\text{CoX}_3 \cdot 6\text{NH}_3$ on treatment with acids. The persistence of a strongly bound unit, $[\text{Co}(\text{NH}_3)_6]^{+++}$, throughout the reactions is clear, and it must be inferred that this unit forms a complex cation, so that the luteocobaltic chloride should be formulated as $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$, and is systematically named hexammine cobaltic chloride. In agreement with this, the Van 't Hoff coefficient i has been determined cryoscopically as 3.9–4.2, and the equivalent conductivity $\Lambda_{1024} = 432$. This, as may be seen by comparison with Table 1, accords with the value expected for a salt dissociating into four ions.

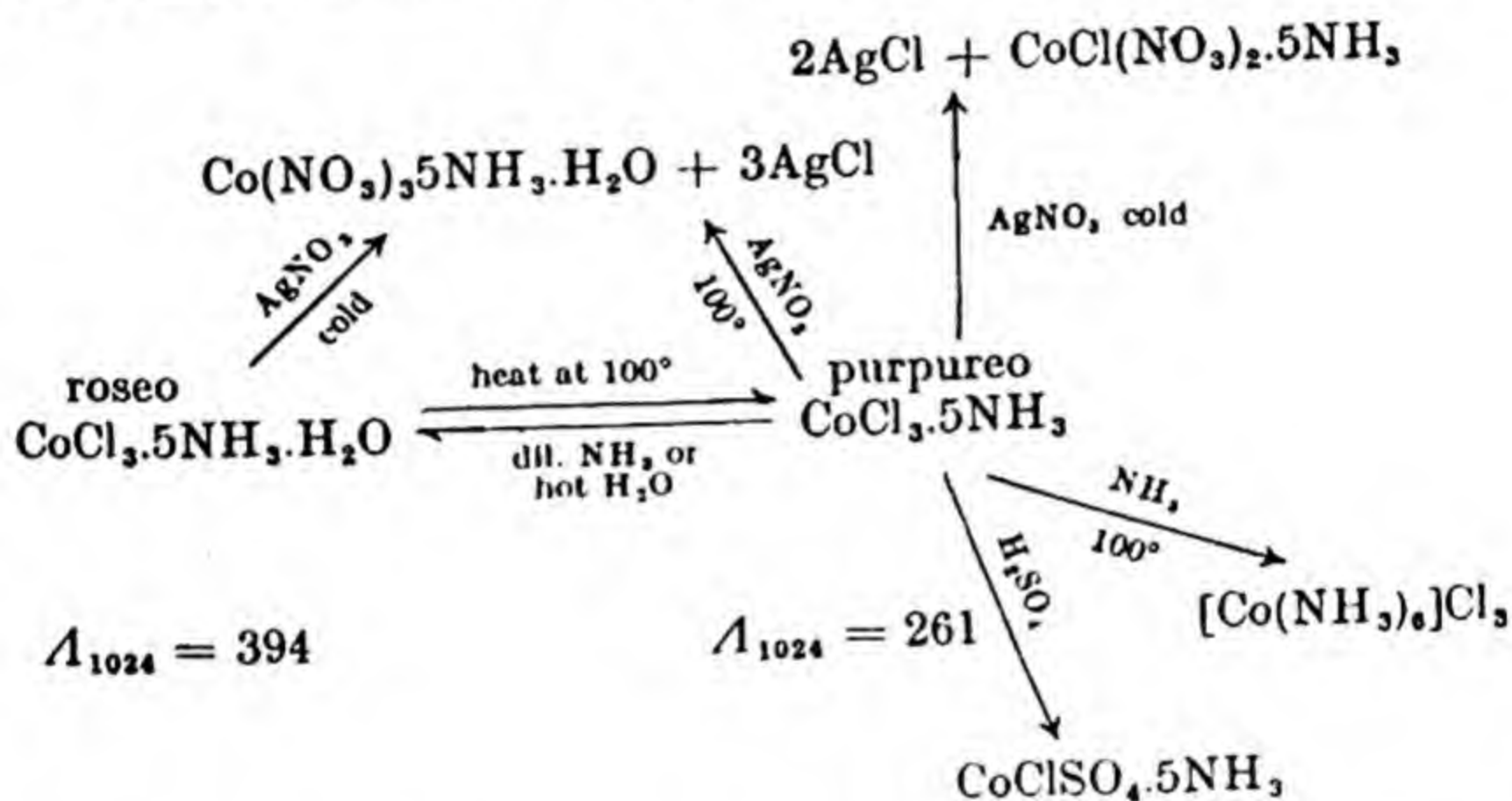
Table 1

Dilution	Salts forming two ions			Salts forming three ions		
	NaCl Λ	KClO_4 Λ	AgNO_3 Λ	BaCl_2 Λ	MgBr_2 Λ	K_2SO_4 Λ
128	113	122	126	224	215	246
256	115	125	128	237	223	257
512	117	126	130	248	230	265
1024	118	127	131	260	235	273

Dilution	Salts forming four ions			Salts forming five ions	
	AlCl_3 Λ	CeCl_3 Λ	$\text{K}_3\text{Fe}(\text{CN})_6$ Λ	$\text{K}_4\text{Fe}(\text{CN})_6$ Λ	$[\text{Pt}(\text{NH}_3)_5]\text{Cl}_2$ Λ
128	342	366	372	432	—
256	371	381	397	477	433
512	393	393	418	520	485
1024	413	408	435	558	523

A second salt obtainable by the oxidation of cobalt chloride in presence of ammonia is the compound $\text{CoCl}_3 \cdot 5\text{NH}_3 \cdot \text{H}_2\text{O}$, long known as *roseocobaltic chloride*. From this there may be made other salts—e.g. a sulphate $\text{Co}_2(\text{SO}_4)_3 \cdot 10\text{NH}_3 \cdot 5\text{H}_2\text{O}$, a chlorplatinate $\text{Co}_2(\text{PtCl}_6)_3 \cdot 10\text{NH}_3 \cdot 8\text{H}_2\text{O}$, etc. On dehydration at room temperature, these salts lose $3\text{H}_2\text{O}$ and $6\text{H}_2\text{O}$, respectively, whereas the chloride suffers no loss of water, indicating that in all of them one molecule of water per atom of cobalt is differently, and more firmly, bound than the rest. Since this molecule of water, in company with

5NH_3 , appears in all the salts, it is to be inferred that it is a constituent of a complex cation, $\left[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}\right]^{3+}$, exactly analogous to the hexammine cobaltic cation, but with one molecule of ammonia replaced in the co-ordination shell itself by a molecule of water, thereby maintaining the co-ordination number 6. Roseocobaltic chloride is therefore termed aquopentammine cobaltic chloride. This view is completely substantiated by the chemical properties of the salt, since all the chlorine is immediately precipitated by silver nitrate, while $\Lambda_{1024} = 394$, so that the salt dissociates into four ions. Finally, a distinction is drawn between the water of crystallization of the salts, which is readily lost over sulphuric acid at room temperature, and the more tenaciously held complex-water. This last molecule may, indeed, be removed at 100° , but by its removal a new salt with different properties is produced.

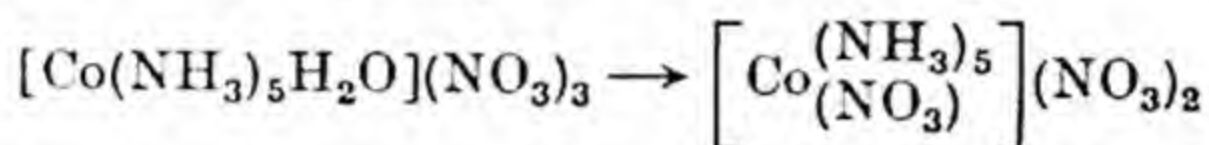


The salt obtained by dehydration of aquopentammine cobaltic chloride at 100° proves to be identical with the purpureocobaltic chloride $\text{CoCl}_3 \cdot 5\text{NH}_3$ produced by the direct oxidation of ammoniacal cobalt salts. In this compound, it was very early observed that two chlorine atoms differ from the third, since silver nitrate, in cold solution, precipitates only two atoms of chlorine (Krok, 1870), leaving in solution a salt from which the remaining chlorine is precipitated slowly on boiling. Similarly, concentrated sulphuric acid forms a sulphate $\text{CoClSO}_4 \cdot 5\text{NH}_3$, which does not react with silver nitrate. Since the equivalent conductivity shows that the purpureo chloride dissociates into three ions, it is clear that the inertness of the third chlorine atom is to be accounted for by its incorporation in the co-ordinated complex, forming a new type of

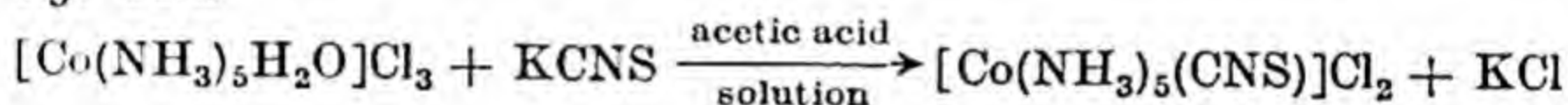
complex cation, $\left[\text{Co} \begin{smallmatrix} (\text{NH}_3)_5 \\ \text{Cl} \end{smallmatrix} \right]^{2+}$, related to the hexammine cation $[\text{Co}(\text{NH}_3)_6]^{3+}$ by the replacement of one neutral molecule of ammonia by a negative chloride ion which is not dissociated off electrolytically. While maintaining the co-ordination number 6, the entry of a negative ion into the co-ordinated complex has the effect of reducing by one unit the nett cationic charge, making the whole bivalent. On Werner's nomenclature, the compound is named systematically as a *chloropentammine cobaltic* salt.

The place of the chloride ion inside the complex may be taken by other anions, which may be introduced in general by one or other of two reactions:

(a) The displacement of water from the corresponding aquopentammine salt by heating above 100° : *e.g.*

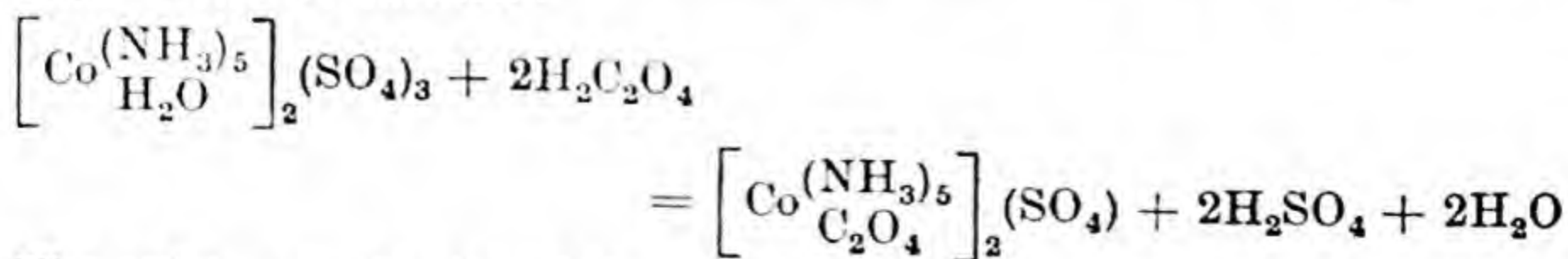


(b) From aquopentammine salts in mildly acid solution, especially with those anions with a strong tendency to complex ion formation—*e.g.* CNS'



Ionization Isomerism.—It is important to note that in certain cases dibasic acid radicals may occupy only one position in the co-ordinated complex. Thus, by the action of concentrated sulphuric acid upon chloropentammine cobaltic chloride, an acid sulphate is obtained having the composition $\text{CoSO}_4 \cdot \text{SO}_4\text{H} \cdot 5\text{NH}_3 \cdot 2\text{H}_2\text{O}$, in which the bisulphate group alone may readily be exchanged for other acids. This leads to the formulation $\left[\text{Co} \begin{smallmatrix} (\text{NH}_3)_5 \\ \text{SO}_4 \end{smallmatrix} \right] \text{SO}_4\text{H} \cdot 2\text{H}_2\text{O}$, which is substantiated by the equivalent conductivity of the corresponding bromide, $\Lambda_{1024} = 114$, indicating dissociation into two ions only. While occupying only one co-ordination position and being un-ionized, the SO_4 group neutralizes two of the ionic charges upon the cobalt, making the whole complex ion univalent.

Other dibasic acids may behave similarly; thus, by the action of oxalic acid on aquopentammine cobaltic salts, an oxalatopentammine series is formed:



The existence of salts of the type described opens up the possibility

of a new type of isomerism which does, in fact, occur, and which Werner termed *ionization isomerism*. Thus, the violet red sulphatopentammine bromide $\left[\text{Co} \begin{smallmatrix} (\text{NH}_3)_5 \\ \text{SO}_4 \end{smallmatrix} \right] \text{Br}$ is an ionization isomer of the violet bromopentammine sulphate $\left[\text{Co} \begin{smallmatrix} (\text{NH}_3)_5 \\ \text{Br} \end{smallmatrix} \right] \text{SO}_4$.

Salt Isomerism.—A second important type of isomerism occurring in the acidopentammine series is that termed *salt isomerism*, which is associated with the potential existence of isomeric forms of the acid radical bound within the complex.

The oxidation of ammoniacal cobalt sulphate with nitrous gases leads to the formation of a brownish-yellow salt, xanthocobaltic sulphate, $\text{Co}(\text{NO}_2)\text{SO}_4 \cdot 5\text{NH}_3$, which is stable towards mineral acids, and which is converted by dilute nitric acid to the nitrate $\text{Co}(\text{NO}_2)(\text{NO}_3)_2 \cdot 5\text{NH}_3$. The corresponding chloride has $\Lambda_{1024} = 240$, and so dissociates into three ions, implying that the xanthocobaltic salts are the salts of a complex cation $\left[\text{Co} \begin{smallmatrix} (\text{NH}_3)_5 \\ \text{NO}_2 \end{smallmatrix} \right]$, containing a stable $-\text{NO}_2$ group.

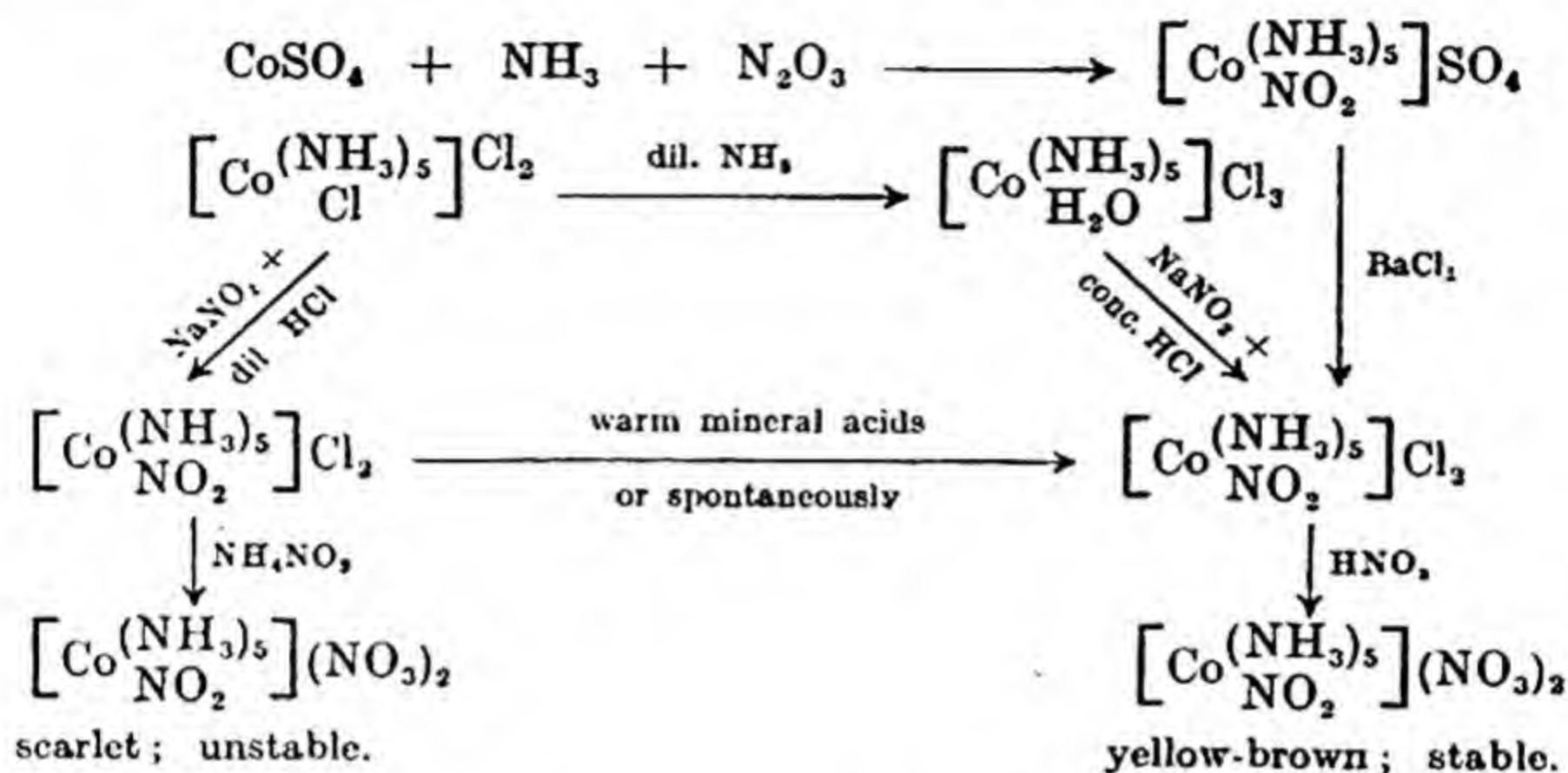
An isomeric salt may be prepared by treating a neutral solution of aquopentammine cobaltic chloride with sodium nitrite. A reddish-chamois coloured chloride, $\text{Co}(\text{NO}_2)\text{Cl}_2 \cdot 5\text{NH}_3$, is thus obtained, from which a scarlet nitrate $\text{Co}(\text{NO}_2)(\text{NO}_3)_2 \cdot 5\text{NH}_3$ is precipitated by means of ammonium nitrate. That these are also salts of a cation $\left[\text{Co} \begin{smallmatrix} (\text{NH}_3)_5 \\ \text{NO}_2 \end{smallmatrix} \right]$ is confirmed by the equivalent conductivity $\Lambda_{1024} = 258$ for the chloride. The red salts are, however, unstable, and are immediately converted by the action of warm mineral acids, or more slowly in aqueous solution or in the solid state, into salts of the xantho series. The relation between the two series is summarized in the table on the next page.

The only apparent seat of isomerism is in the $-\text{NO}_2$ group, which might—as in the organic nitrous esters and nitro compounds

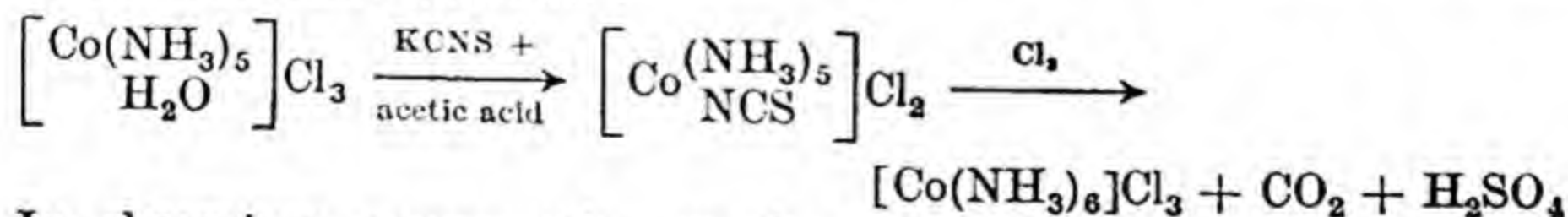
—react either as $-\text{O}-\text{N}=\text{O}$, or as $-\text{N} \begin{smallmatrix} \text{O} \\ \text{O} \end{smallmatrix}$. Such isomerism is

not known amongst the inorganic nitrites. The xantho salts are the more stable series, and are yellow in colour, as is the hexammine cobaltic cation, in which only nitrogen atoms are linked to the cobalt. Aquopentammine cobaltic chloride $\left[\text{Co} \begin{smallmatrix} (\text{NH}_3)_5 \\ \text{OH}_2 \end{smallmatrix} \right] \text{Cl}_3$ and nitritopentammine cobaltic chloride $\left[\text{Co} \begin{smallmatrix} (\text{NH}_3)_5 \\ \text{ONO} \end{smallmatrix} \right] \text{Cl}_2$, in both

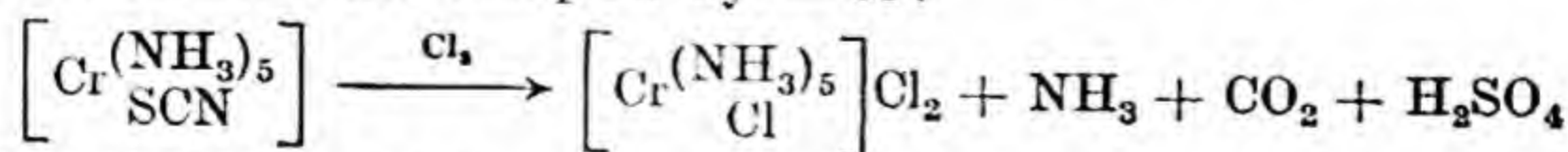
of which cobalt is undoubtedly linked to one oxygen atom, are red. Hence, reasoning both from colour and from stability, the red salts are regarded as *nitritopentammine* salts, $\left[\text{Co} \begin{smallmatrix} (\text{NH}_3)_5 \\ \text{ONO} \end{smallmatrix}\right] \text{X}_2$, and the xantho salts as *nitropentammines*, $\left[\text{Co} \begin{smallmatrix} (\text{NH}_3)_5 \\ \text{NO}_2 \end{smallmatrix}\right] \text{X}_2$. In all cases, the nitro compounds are the stable isomers.



Salt isomerism might be expected to occur also with thiocyanato compounds, in which either the true thiocyanato ion, $-\text{S}-\text{C}\equiv\text{N}$, or the isothiocyanato ion, $-\text{N}=\text{C}=\text{S}$, might be involved. Such isomerism does not occur, however, although compounds of both types are known. In cobaltammines, the group is invariably present in the isothiocyanato form, since hydrolytic oxidation with chlorine leaves the nitrogen still attached to the cobalt atom, in the form of an ammonia molecule:



In chromium compounds, on the other hand, the normal thiocyanato group is present, since on similar treatment $-\text{SCN}$ is replaced inside the complex by $-\text{Cl}$:



Disubstituted Complexes.—In harmony with Werner's conception of the equivalence of the co-ordination positions, it has been seen that complex ions of the type $[\text{CoA}_5\text{B}]$, where A is, *e.g.*, NH_3 ,

and B may be either a neutral molecule such as H_2O , or an acid radical, exist only in one form except where salt isomerism occurs. The substitution of a second group, giving a complex of the type $[\text{CoA}_4\text{XY}]$, must lead to the possibility of *stereoisomerism*, and the number of isomers formed should indicate the spatial arrangement of the groups. Of the three possible arrangements of six equivalent points (Fig. 27), both the plane hexagonal (i) and the trigonal prismatic (ii) arrangements should lead to three isomers of $[\text{CoA}_4\text{XY}]$, in which X and Y occupy the relative positions 1,2, 1,3, and 1,4, respectively. A regular octohedral arrangement (iii) leads to two disubstituted products—1,2 and 1,6—and only two trisubstituted products $[\text{CoA}_3\text{X}_3]$ (Fig. 28). Experiment shows the existence of two stereoisomers in each case, and fully confirms Werner's theory of the octohedral arrangement of the 6-co-ordinated complex, as will be seen.

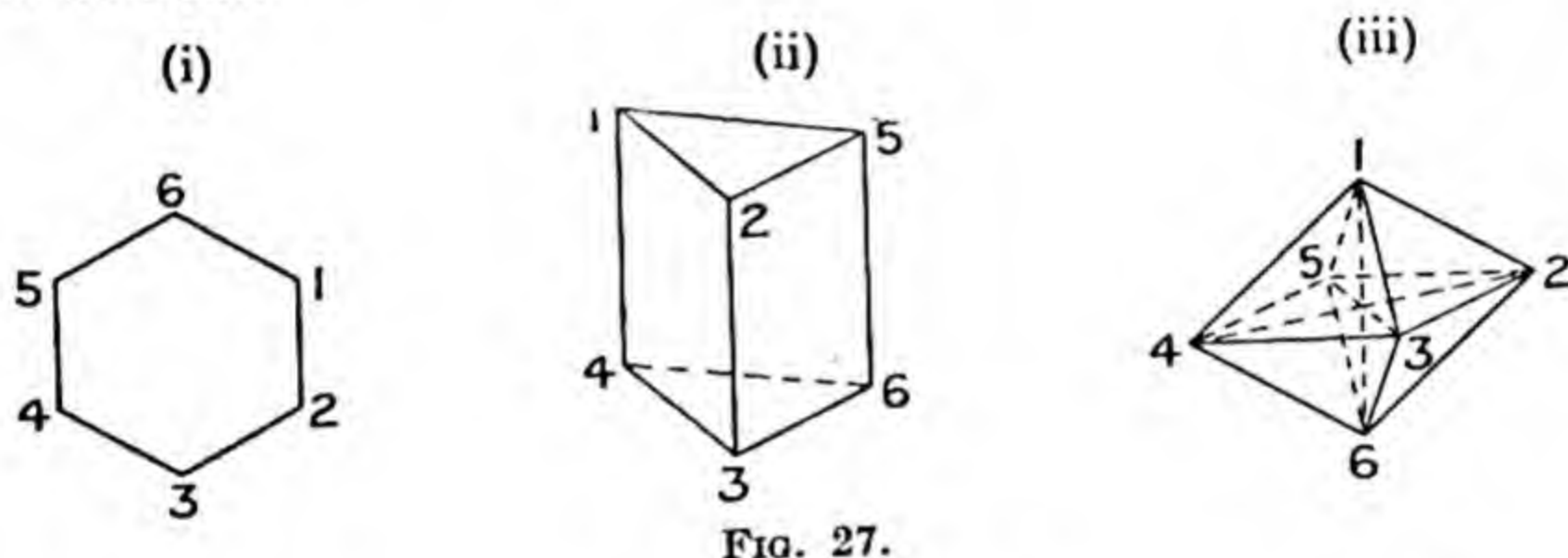


FIG. 27.

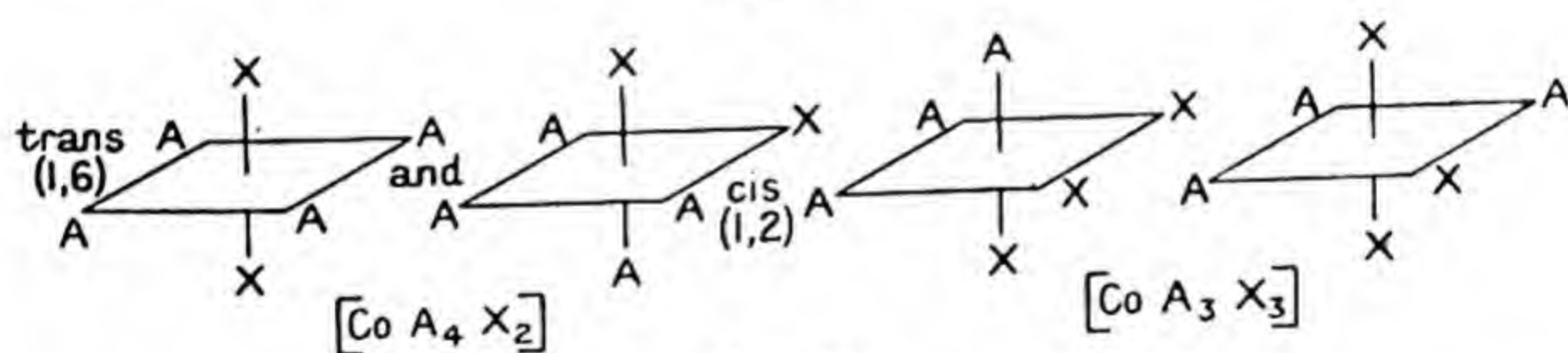
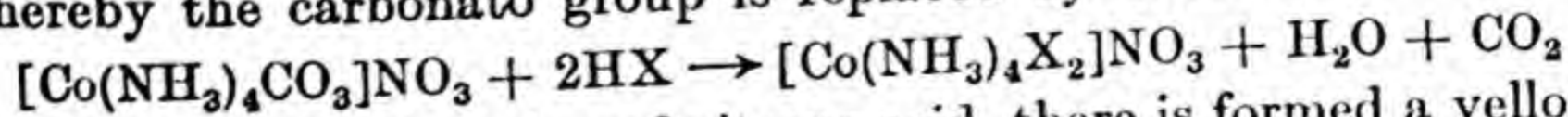


FIG. 28.

Cis-trans Isomerism in Diacidotetrammine Complexes.—

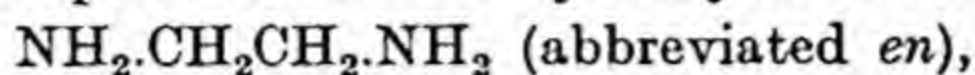
The oxidation of cobaltous salts in the presence of ammonium carbonate gives rise to a salt which, from its reactions, is a carbonatotetrammine cobaltic salt, $[\text{Co}(\text{NH}_3)_4\text{CO}_3]\text{X}$. This reacts readily with acids, whereby the carbonato group is replaced by other acid radicals:



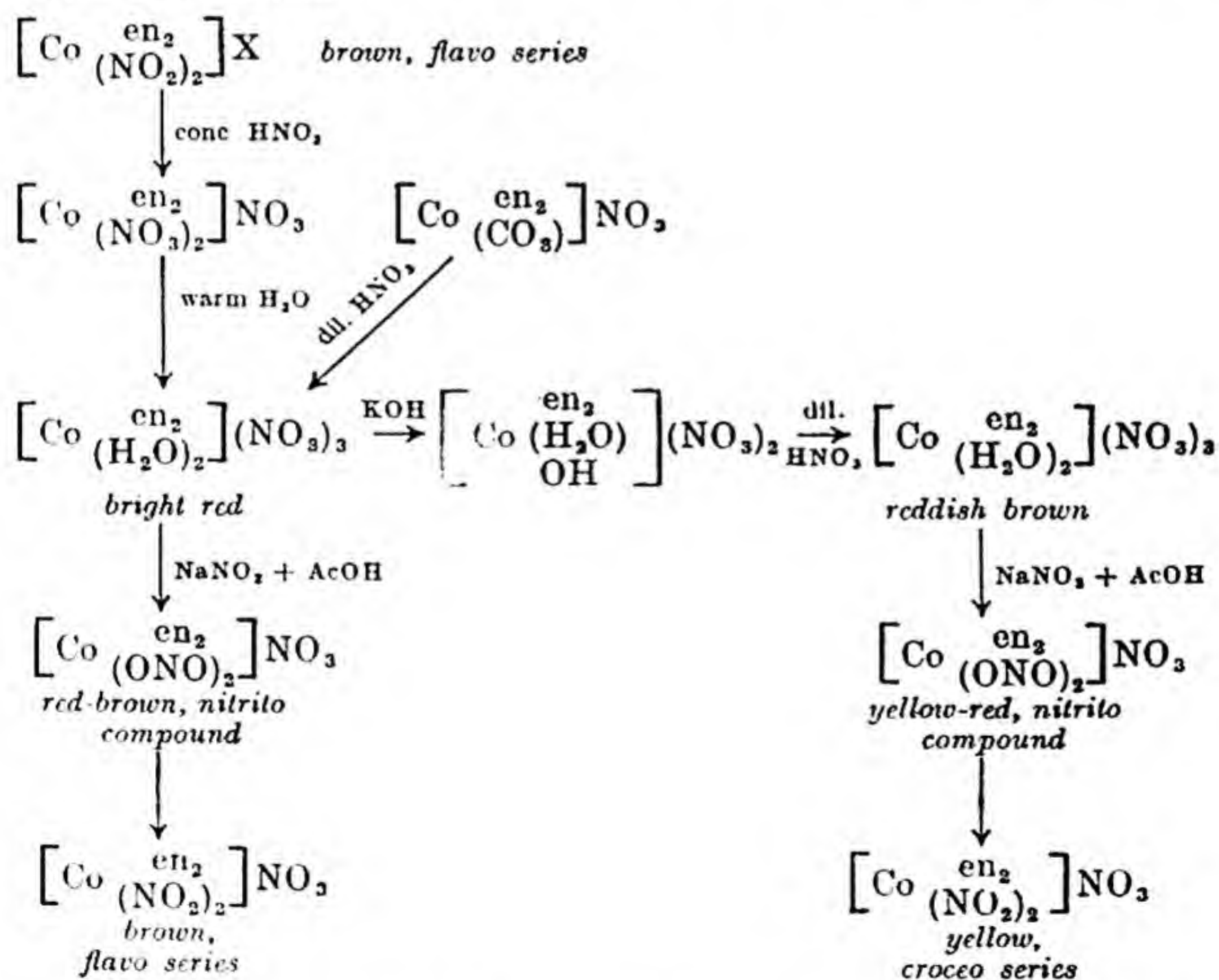
In this way, by the action of nitrous acid, there is formed a yellow-brown salt, $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]\text{NO}_3$, flavocobaltic nitrate, which has $A_{1024} = 101$. An isomeric salt, croceocobaltic nitrate, is formed

by the oxidation of cobaltous salts in the presence of sodium nitrite, or by the action of sodium nitrite and acetic acid upon $[\text{Co}(\text{NH}_3)_5\text{NO}_2](\text{NO}_3)_2$. This croceo salt is orange-yellow in colour, and has $\lambda_{1024} = 88$. That both flavo and croceo salts are nitro compounds is shown by their stability towards acids. Hence, since both salts dissociate into two ions, their differences must be attributed to stereoisomerism.

The same type of isomerism is shown in the dinitro-diethylenediamine cobaltic salts, the reactions of which show, indeed, that two isomeric series of all disubstituted complexes may be prepared. The complex compounds formed by ethylenediamine,



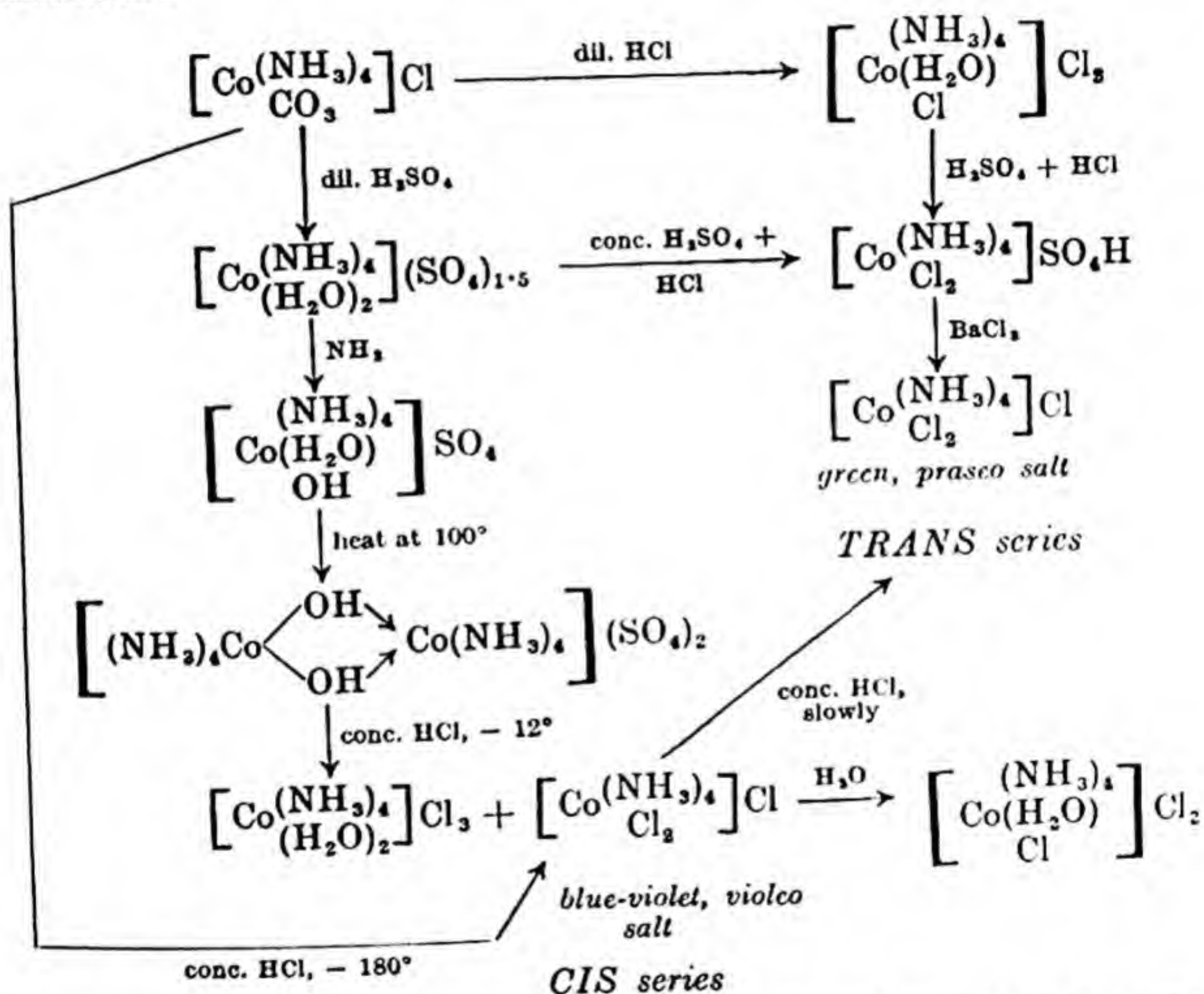
which fills the place of two molecules of ammonia, exactly resemble the amines. In general, the introduction of ethylenediamine increases the stability of the compounds. The relation between the stereoisomeric series of compounds is shown by the following series of reactions :



The Determination of Configuration.—Determinations of the configuration of stereoisomeric series depend on the fact that

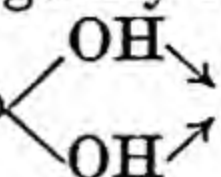
bifunctional groups, such as ethylene diamine or the oxalate ion (called by G. T. Morgan '*chelate*' groups, after the Greek $\chi\eta\lambda\acute{\eta}$, a crab's claw), can, from considerations of molecular dimensions, span only *cis*, or 1,2 positions. Hence, provided that no intramolecular change of configuration occurs during reaction, the isomer which is capable of reacting with a chelating group, or which is formed by displacement of such a group, must belong to the *cis* series.

The application of this reasoning to the isomeric dichlorotetrammine cobaltic salts is summarized in the following series of reactions :



In this case, the determination of configuration involves the binuclear complex $\left[(\text{NH}_3)_4\text{Co} \begin{pmatrix} \text{OH} \\ \text{OH} \end{pmatrix} \text{Co}(\text{NH}_3)_4 \right] (\text{SO}_4)_2$. Just as, in the aquopentammine salts, the loss of water introduces an acid radical into the co-ordinated complex, so by the dehydration of a *cis* hydroxo-aquo salt, such as $\left[\text{Co} \begin{pmatrix} \text{NH}_3 \\ \text{H}_2\text{O} \\ \text{OH} \end{pmatrix}_4 \right] \text{SO}_4$, a polynuclear

complex is formed. We may regard the *di-ol octammine dicobaltic sulphate* here formed as being constituted exactly analogously to the

ethylenediamine compounds, with the group $(\text{NH}_3)_4\text{Co}$  act-

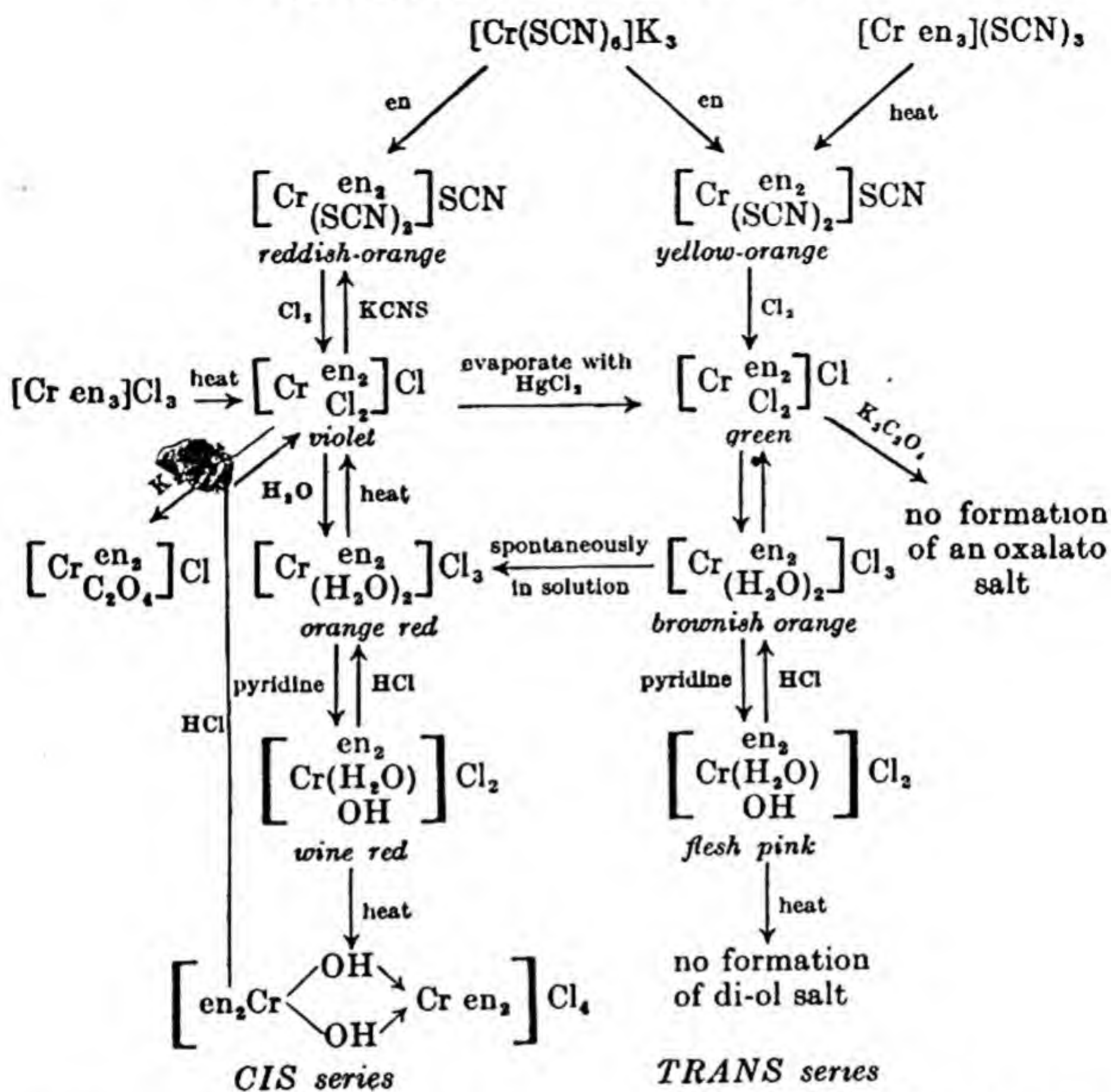
ing as a chelating group, and filling two co-ordination positions around the second cobalt atom. In principle, therefore, it does not differ from the other chelate groups already referred to, so that the violeo chloride obtained by fission of the binuclear complex must belong to the *cis* series. It is important to observe, however, that the action of concentrated hydrochloric acid upon carbonato-tetrammine cobaltic chloride, except under extreme conditions, leads to a change of configuration; alcoholic hydrochloric acid yields a mixture of violeo and praseo chloride, while the violeo chloride itself undergoes slow conversion to the praseo compound in the presence of hydrochloric acid.

The validity of these stereochemical deductions from the octohedral theory is not peculiar to cobalt, as is shown by the existence also of isomeric series of 6-co-ordinate compounds of chromium, platinum and iridium. The reactions of these compounds indicate the same sort of *cis-trans* isomerism as has been seen to exist in the cobaltamines.

Thus, by the action of ethylenediamine upon potassium chromi-thiocyanate, there are formed two compounds of the formula $[\text{Cr}^{\text{en}_2}(\text{SCN})_2]\text{CNS}$, which are shown by the following sequence of reactions to belong to the *cis* and the *trans* series, respectively.⁶ It may be seen that the deeper coloured series gives rise both to the di-ol polynuclear salt, and to an oxalato derivative. Hence, the compounds of this series are shown unequivocally to be the 1,2 compounds. At the same time, the possibility of configurational changes is demonstrated. It will be seen that the *trans*-diaquo salt changes spontaneously into the *cis* compound in solution, whereas the reverse change is brought about by evaporating the *cis*-dichloro complex to dryness with mercuric chloride. This change is brought about, without doubt, by the greater insolubility of the *trans*-dichloro-diethylenediamine chromic mercurichloride. In the absence of mercuric chloride the two dichloro complexes may be heated with hydrochloric acid, or in the solid state at 160°, without any sign of interconversion. The alternative course of elimination of ethylenediamine from the triethylenediamino-chromic chloride and thiocyanate, respectively, is also noteworthy.

Triacidotriammine Complexes.—In the foregoing sections,

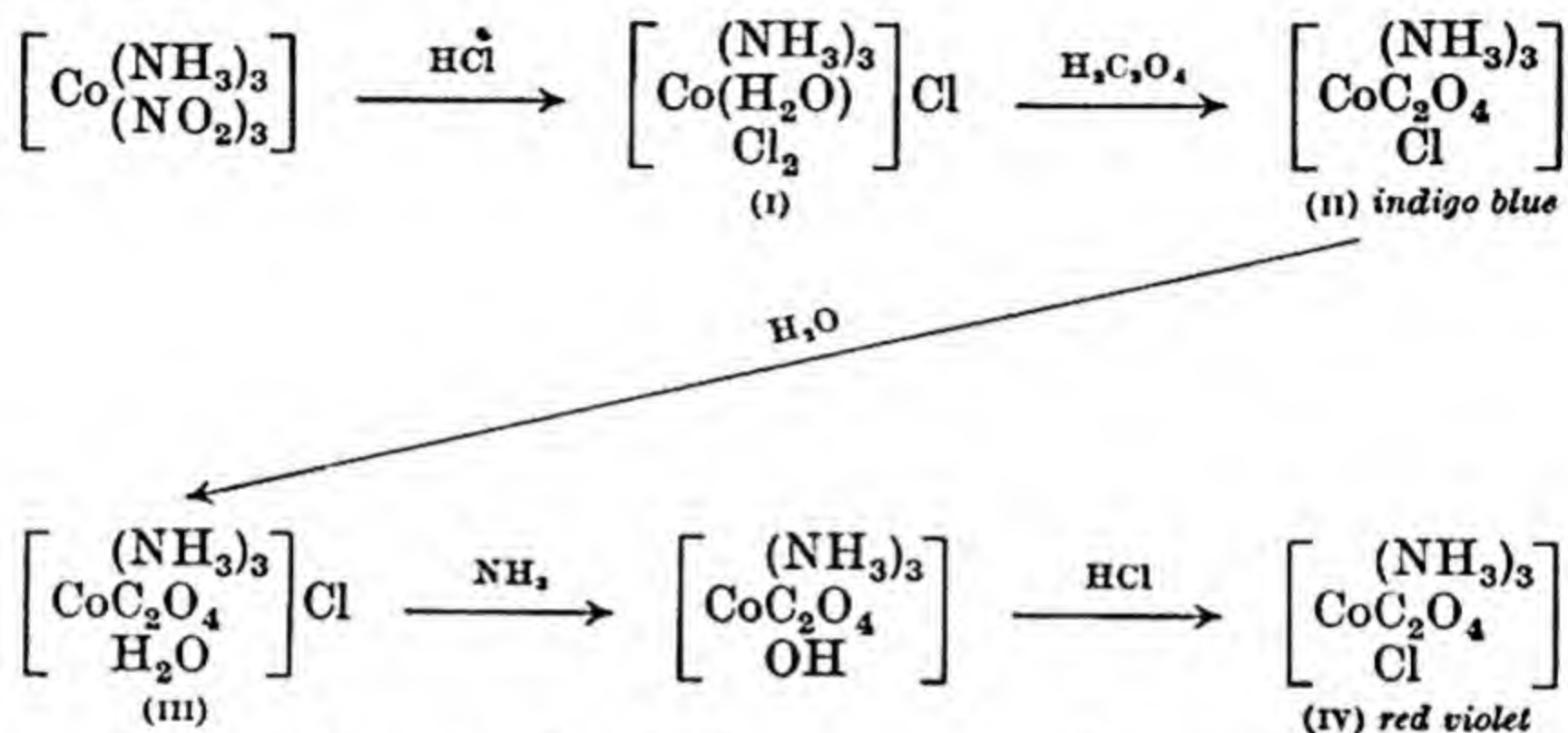
⁶ Pfeiffer, *Ber.*, 1904, 37, 4205.



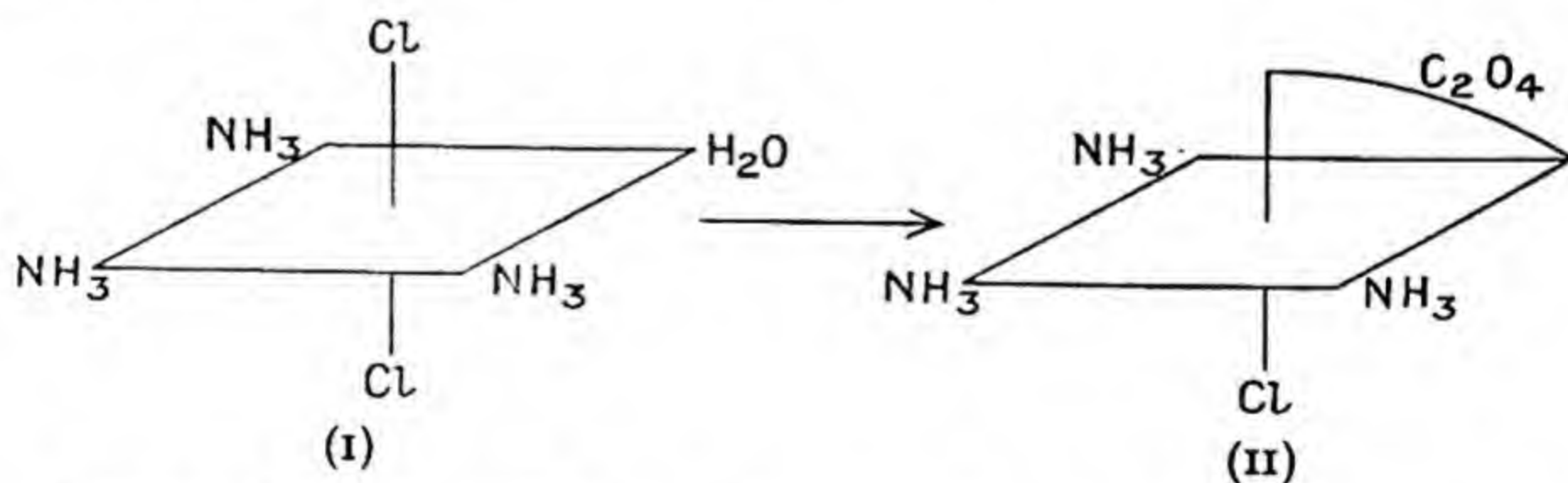
acidopentammine and diacidotetrammine compounds have been discussed. It is clear that the introduction into the co-ordinated complex of a third acid radical, in place of a molecule of ammonia, should lead to the formation of an un-ionized compound. This is found to be the case. One of the products of the oxidation of cobaltous salts in the presence of sodium nitrite and ammonia is a yellow-brown sparingly soluble compound, which is trinitrotri-amine cobalt, $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$. In keeping with this formula, the substance is stable towards acetic acid, and its aqueous solution has $\Lambda'_{1024} = 1.6$. Even this low electrical conductivity may well be due to contamination with electrolytes. Compounds with other acid radicals in the complex, in place of the nitro groups, may also be prepared, and are also, in every case, non-electrolytes.

On the octohedral theory, such trisubstituted complexes should

be capable of existing in two geometrically isomeric forms. In a few cases this is known to be so, although the configuration of the isomers has not in any case been rigidly determined. Thus, when trinitrotriammine cobalt is treated with hydrochloric acid, it yields a deep blue, strongly dichroic compound (I), from which an indigo blue oxalato compound (II) may be made. This, like other chloro compounds, undergoes hydration (frequently termed aquotization) in solution (III). From the aquo-oxalato compound (III), a chloro-oxalato compound (IV) may be regenerated; the salt so produced is, however, red-violet in colour, and so is isomeric with (II).



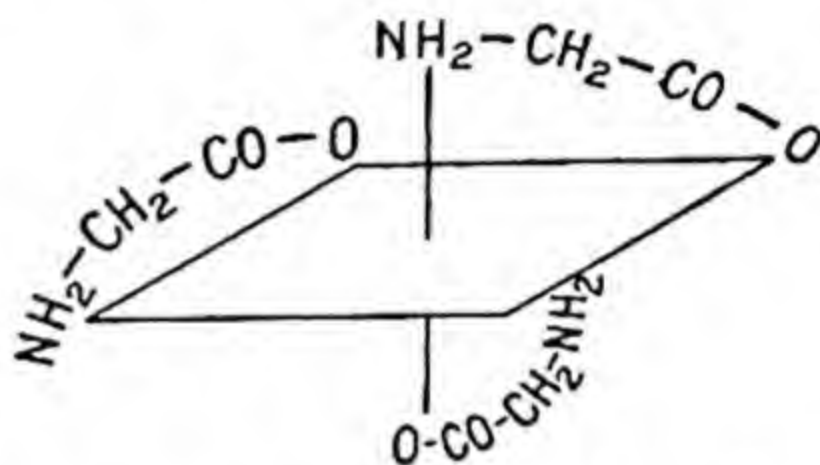
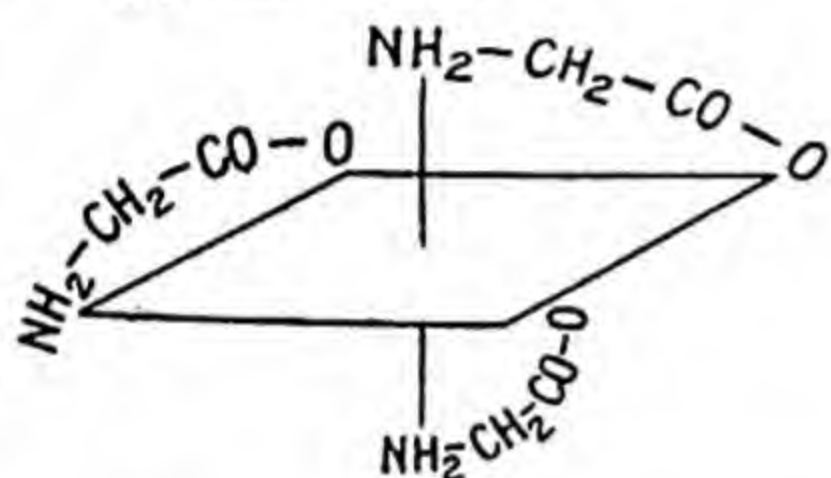
According to Werner, the dichloro compound (I) is the *trans* compound, thereby fixing the configuration of the deep blue chloro-oxalato salt.



Inner Complex Salts.—The non-electrolyte complexes just considered are formed by the attachment of equal numbers of neutral groups and anions to a metallic ion. If the neutral group and acid radical are united in the same molecule—as, for example, in the case of glycine, $\text{NH}_2\text{CH}_2\text{CO}_2\text{H}$ —the compounds formed have, in many cases, great stability, very low solubility in water, but high solubility in organic solvents. Non-electrolyte complexes of

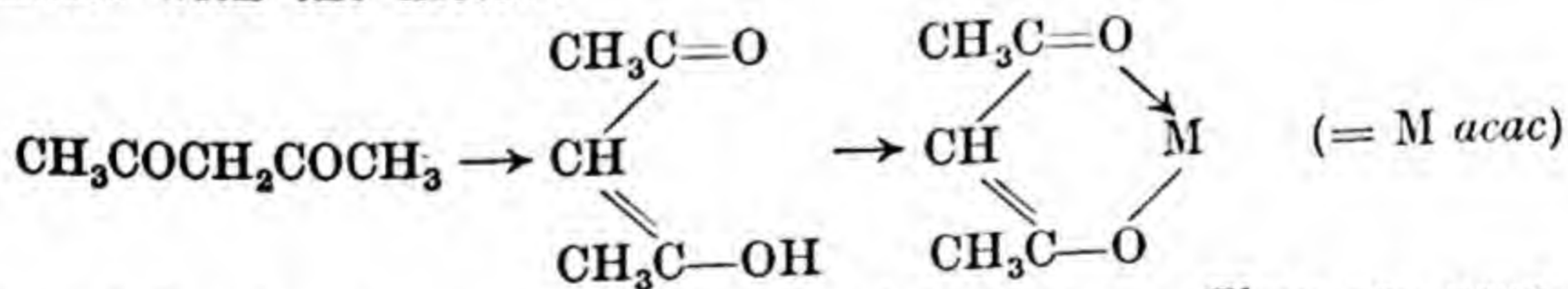
this kind are termed *inner complex salts*. They possess a considerable practical importance in that the formation of such compounds underlies the action of many of the so-called specific analytical reagents, the action of mordant dyestuffs, and many other reactions.

Cobaltic oxide reacts with solutions of glycine forming a mixture of two compounds, having the composition $[\text{Co}(\text{NH}_2\text{CH}_2\text{CO}_2)_3]$, which are remarkably stable. They may be dissolved without change in concentrated sulphuric acid; their aqueous solutions have practically no electrical conductivity; and cryoscopic measurements show that they are undissociated in solution. They therefore represent the two geometrical isomers, predicted by theory, of tris-glycine cobalt:

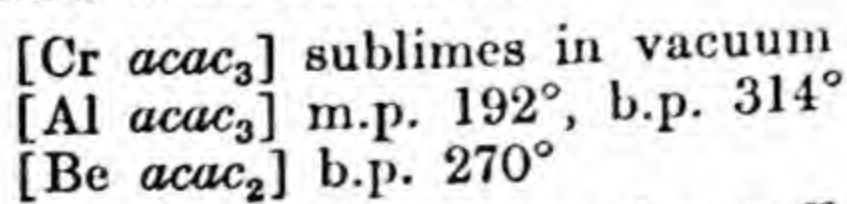


Glycine also forms inner complex salts with other metals; thus copper (co-ordination number 4) forms $\left[\text{Cu} \left(\begin{array}{c} \text{NH}_2\text{CH}_2 \\ | \\ \text{O}-\text{CO} \end{array} \right)_2 \right]$.

A second, particularly important class of inner complex salts is that formed by the enolic form of β -diketones—*e.g.* acetylacetone. The enol group is salt-forming, and the ketonic group then co-ordinates with the metal:

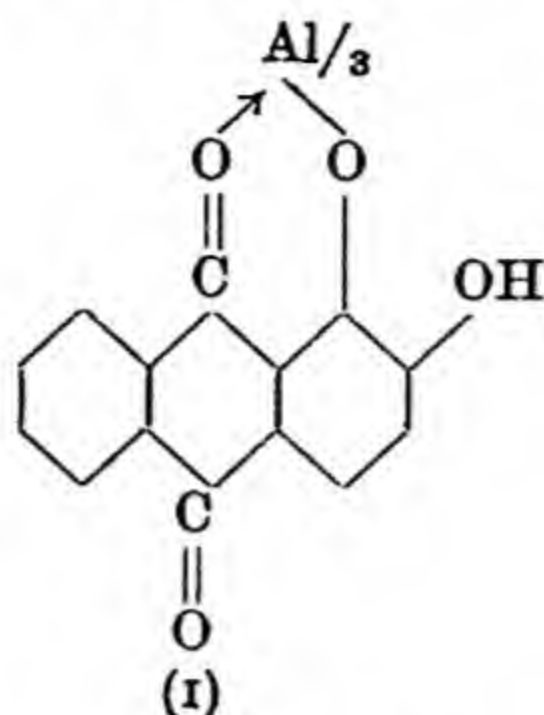


The acetylacetonates are typical non-electrolytes. They are practically insoluble in water, but readily soluble in benzene. Many are low-melting, and even volatile:



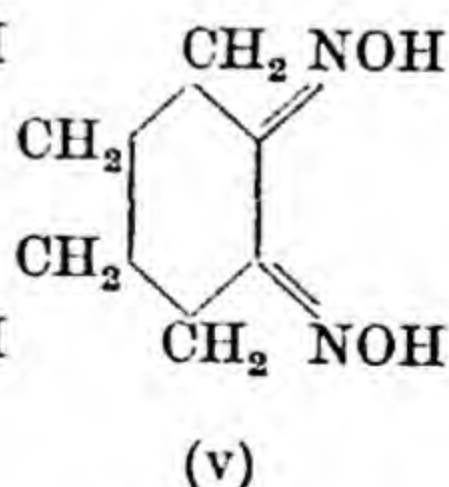
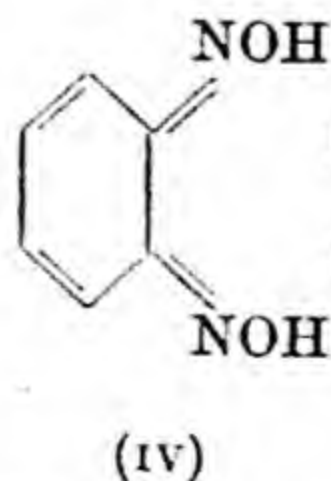
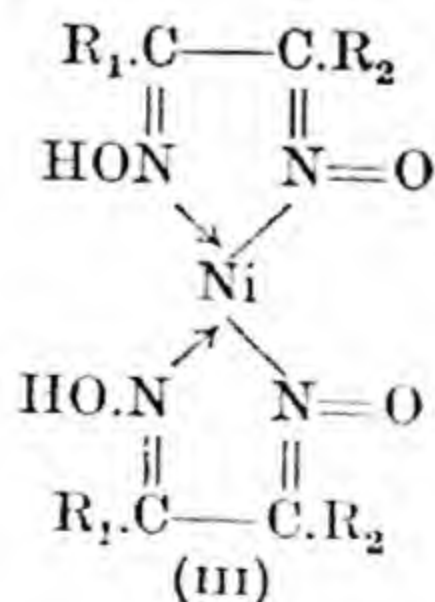
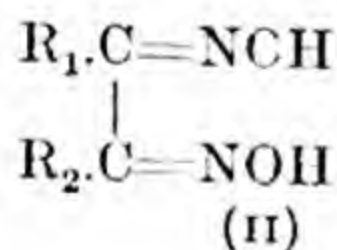
The reaction of hydroxyanthraquinone dyestuffs, such as alizarin, with tin, aluminium, chromium and other metallic mordants, is due to an exactly analogous type of inner complex salt formation. The hydroxyl group in position 1 is salt-forming, and the metal

is co-ordinated to the adjacent carbonyl group, so that the aluminium-alizarin lake may be formulated as (I).



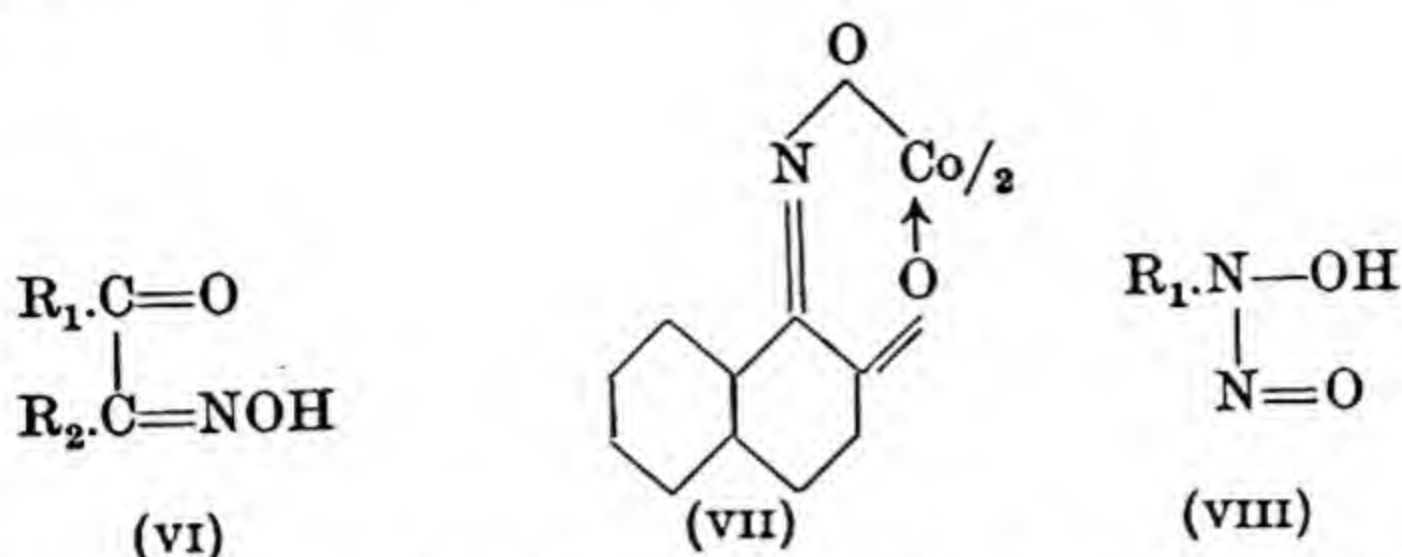
The possibility of inner complex salt formation arises wherever acidic and donor functions (such as the amino-, thiol, or carbonyl groups) are suitably placed in the same molecule, *i.e.* in 1,4 or 1,5 positions to one another. It is a remarkable and quite unexplained phenomenon, however, that the presence of certain atomic groupings may confer the property of forming inner complex salts more or less specifically with some particular metal, *i.e.* the inner complex salt formed by that metal is characterized above all others by its stability and—as a usual corollary—its insolubility in water.

The most familiar instance is the atomic grouping (II), which is specific in this sense for nickel, forming the dialkylglyoxime compounds (III). It is interesting to note that *o*-quinone dioxime (IV) will not give such compounds, although when it is reduced to the corresponding cyclohexane derivative (V) a stable nickel derivative is again formed.



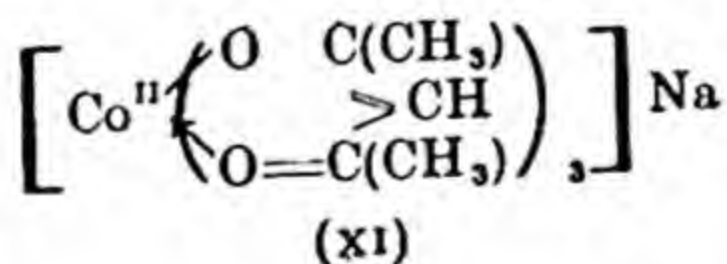
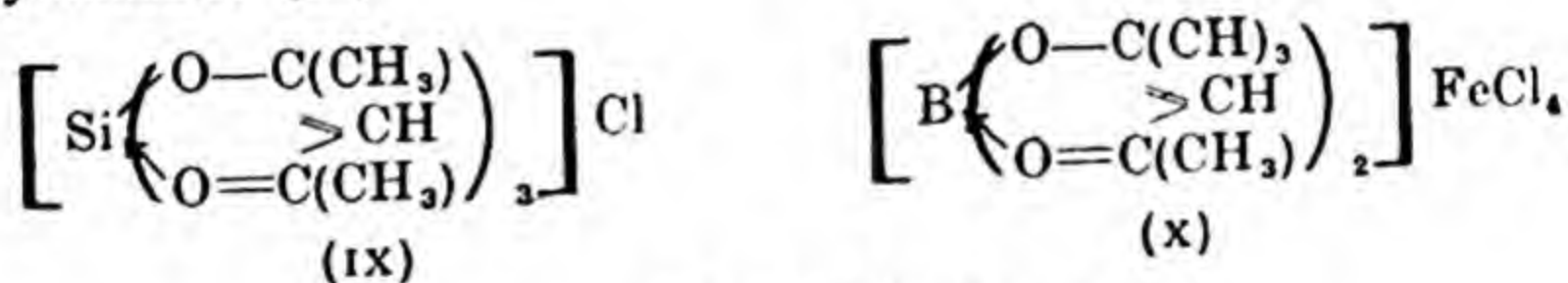
The grouping specific for cobalt is (VI), which in this case is particularly effective when part of a ring structure, as in α -nitroso β -naphthol (oxime form) (VII). In the same way, the grouping

(VIII), present in cupferron $C_6H_5.N(OH).NO$, is weakly specific for iron.



In the cases considered hitherto, the number of acido groups in the inner complex salt has been equal to the valency of the central atom. If this is not the case, the resulting complex will itself be an ion. Compounds of this type were termed by Werner *inner complex salts of the second order*.

Thus, silicon, with the valency four, has a co-ordination number of six. It therefore forms a complex with three molecules of acetylacetone in which one valency of the silicon is unsaturated, since only three acido groups are accommodated inside the complex. The whole therefore forms a unique complex cation containing silicon (IX). In the same way, boron (co-ordination number four, valency three) also forms a complex cation by co-ordination with acetylacetone (X).

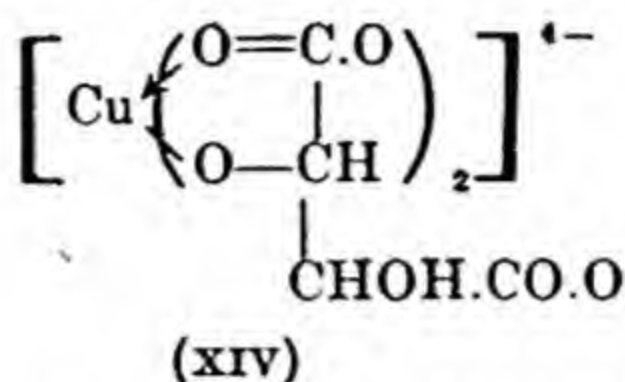
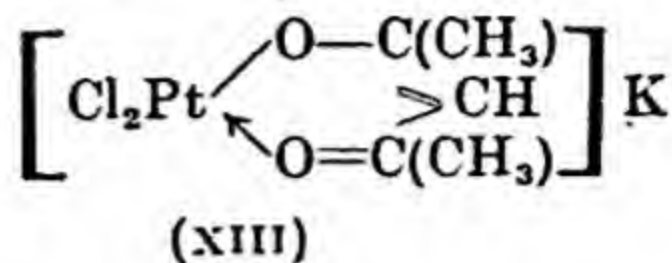
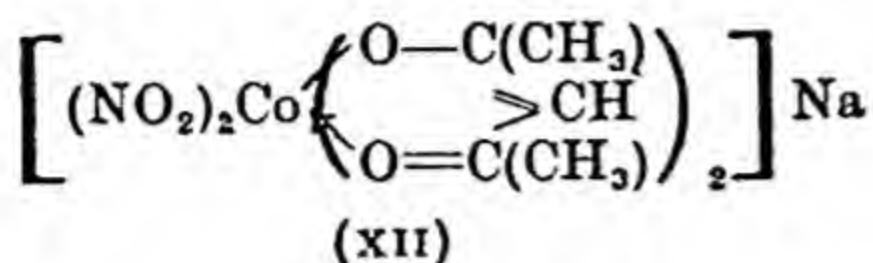


The converse is the case with the acetylacetonate of divalent cobalt (co-ordination number six). The third molecule of acetylacetone required to complete the co-ordination shell confers on the whole complex (XI) anionic properties.

In certain cases, inner complex salts of the second order may be formed when the co-ordination shell is occupied only partially by acetylacetone. Thus, the action of acetylacetone upon sodium cobaltinitrite and potassium chlorplatinate yields the salts (XII) and (XIII), respectively.

The tendency of organic hydroxy-acids to form inner complexes

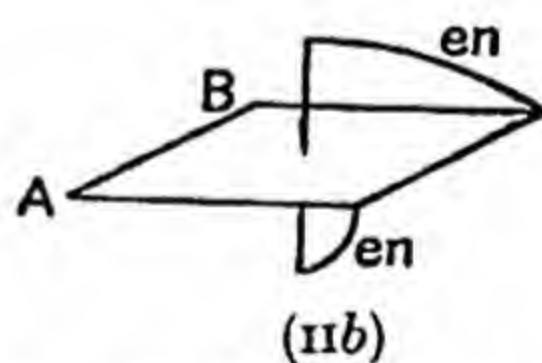
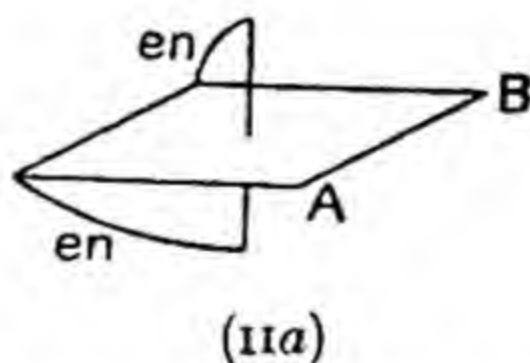
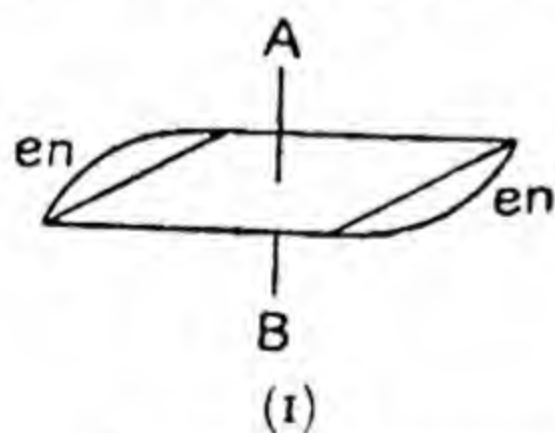
of this kind explains the action of tartaric acid, citric acid, etc., in masking the reactions of the heavy metals. In Fehling's solution, the copper is in this way combined in the cupritartrate ion (XIV),



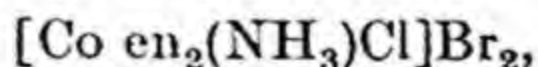
while iron in the presence of citric acid is bound in a binuclear anion $[\text{Fe}_2(\text{C}_6\text{H}_4\text{O}_7)_3]^{6-}$. These complex anions are stable in neutral and ammoniacal solutions, no free ferric or cupric ions being detectable.

Optical Isomerism.—The octohedral configuration of the 6-co-ordinate complex requires the existence not only of geometrical isomerism of the kind discussed in the previous sections, but also of mirror-image isomerism, leading to optical activity.

The *trans* form of a compound $[\text{Co en}_2\text{AB}]$ (I) possesses a plane of symmetry, and so must be non-resolvable. The *cis* form (IIa), however, is not superposable upon its mirror image (IIb), and so should be capable of resolution into optical isomers.



This possibility was experimentally realized in 1911 by Werner,⁷ who resolved the $[\text{Co en}_2(\text{NH}_3)\text{Cl}]^{2+}$ complex by means of its *d*-bromcamphorsulphonate, and found for the bromide



a specific rotation $[\alpha]_D = \pm 43^\circ$.

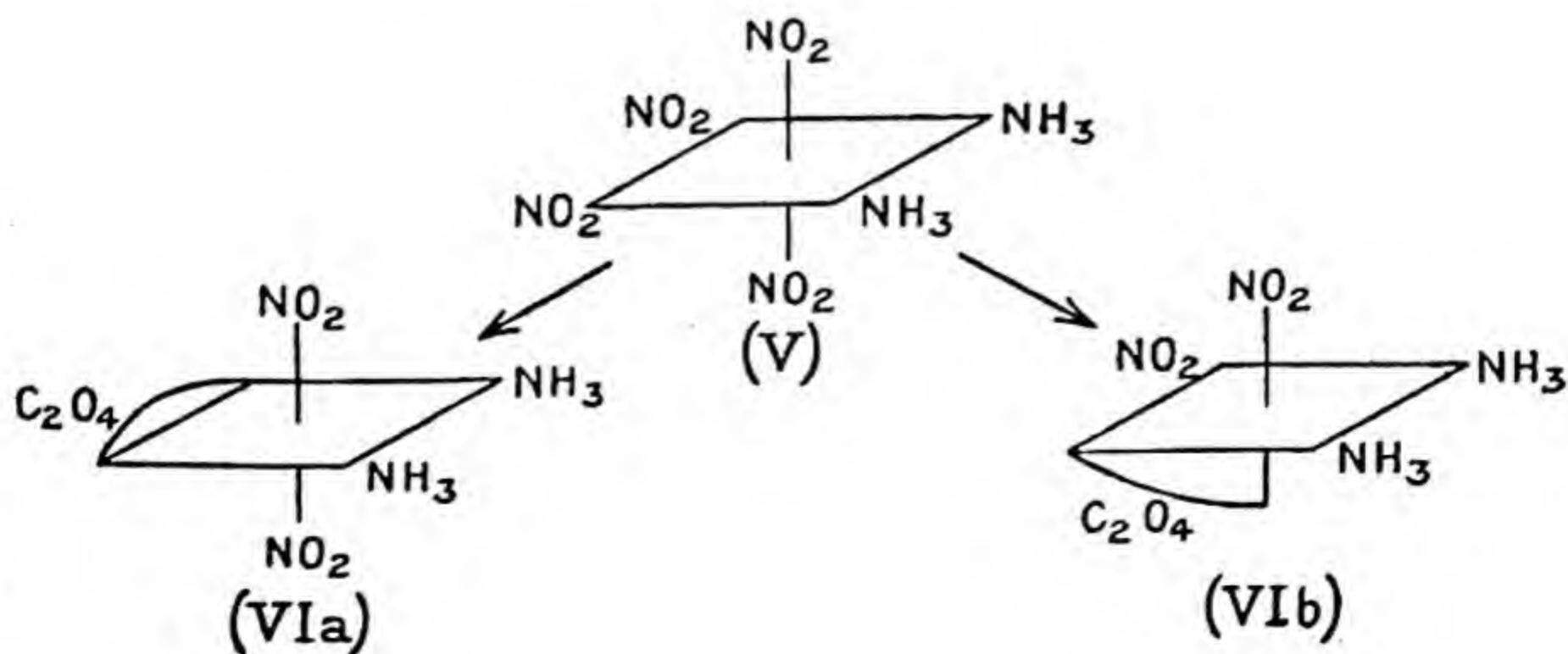
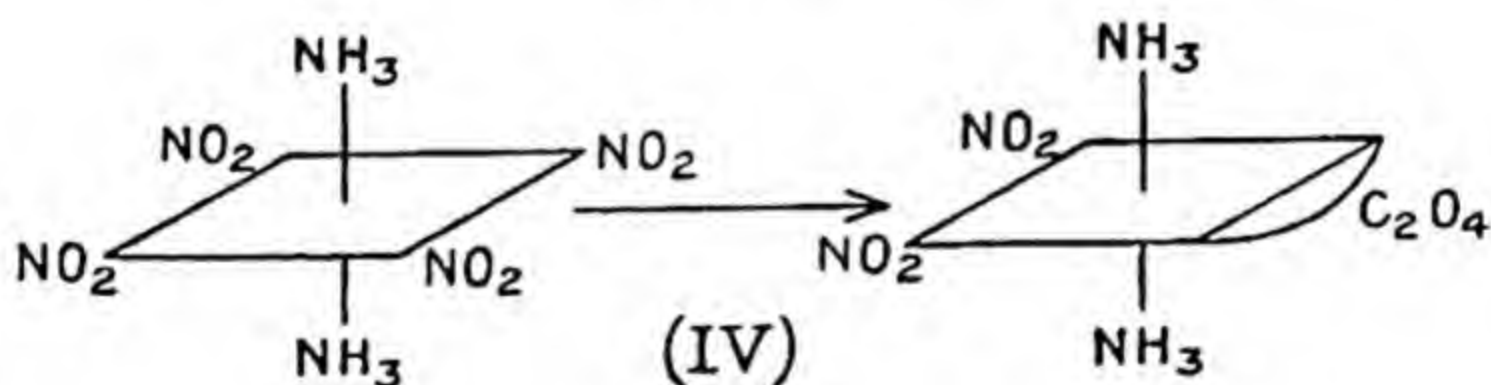
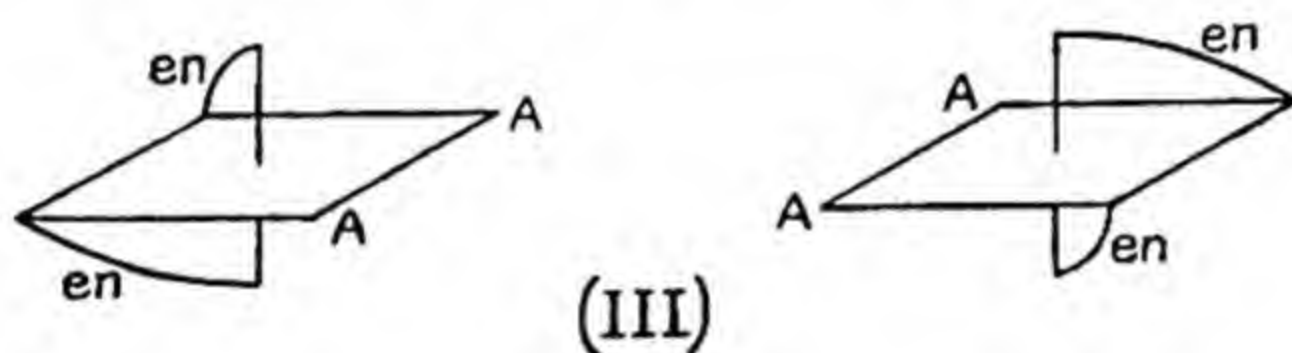
The molecular dissymmetry does not vanish if $A = B$ (III). In fulfilment of this, Werner found⁸ that the violeo salts $[\text{Co en}_2\text{Cl}_2]\text{X}$, and the flavo salts $[\text{Co en}_2(\text{NO}_2)_2]\text{X}$, were resolvable, thereby confirming the determinations of configuration arrived at by other

⁷ Werner, *Ber.*, 1911, 44, 1887.

⁸ Werner, *ibid.*, 44, 2445, 3279.

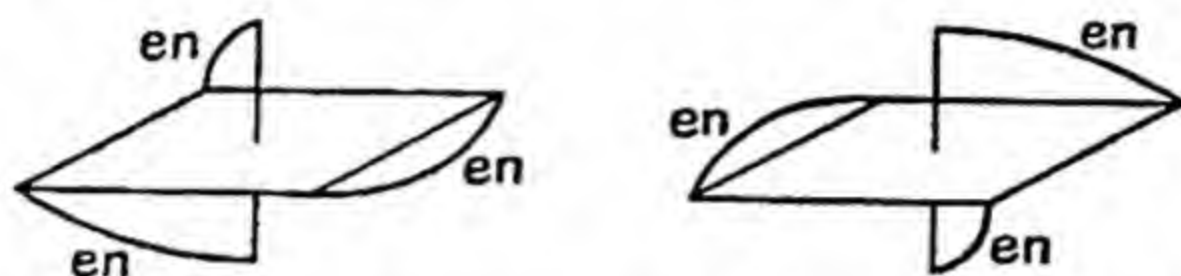
means. In all cases, the series of salts classed, from their reactions, as *trans* compounds proved incapable of resolution. For the maintenance of dissymmetry it is not even necessary that two chelating groups should be present: *cis* compounds of the type $[\text{Co enA}_2\text{B}_2]$ must also display optical activity.

In determining the configuration of a complex ion by indirect means, it has to be assumed that the mechanism of substitution reactions is such that they do not bring about any change of configuration at any stage. This assumption is by no means universally valid. Thus Erdmann's salt, $[\text{Co}(\text{NO}_2)_4(\text{NH}_3)_2]\text{NH}_4$, may be converted to an oxalato compound $[\text{Co}(\text{NO}_2)_2(\text{C}_2\text{O}_4)(\text{NH}_3)_2]\text{NH}_4$, which is of the type discussed above. If this were derived directly from a *trans* tetranitrodiammine (IV), it could not display optical isomerism; if from a *cis* compound (V), two oxalato compounds should be formed, of which one (VIa) has a plane of symmetry, whilst the other (VIb) should be resolvable. Shibata reported that the oxalato dinitro diammine from Erdmann's salt could be resolved



into optical isomers, and concluded that Erdmann's salt has the *cis* structure (V). Nevertheless, X-ray evidence is compatible only with the *trans* structure (IV) for the anion of Erdmann's salt, so that it may be inferred that a change of configuration takes place during the substitution reaction.

The conclusive success of the octohedral model is finally demonstrated by the resolution of the type $[\text{Co en}_3]^{3+}$, in which there is no asymmetry of any one atom, but there exist only 'odd' symmetry elements of the whole molecule, in the form of trigonal axes of symmetry through the centres of the octohedron faces. In

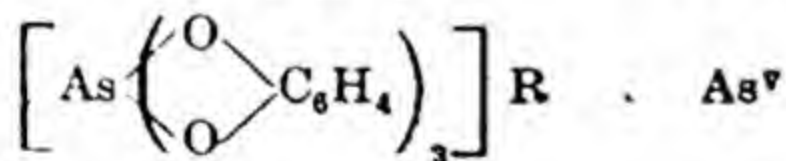


agreement with the requirements of theory, Werner⁹ found that $[\text{Co en}_3]\text{Br}_3$ could be resolved into antimers having $[\text{M}]_D = 600^\circ$. Plainly, the trioxalato complexes $[\text{Co}(\text{C}_2\text{O}_4)_3]\text{M}_3$ must have the same symmetry, and are therefore also resolvable. Since stable compounds of these two types are formed by many metals, their resolution has proved of great importance in establishing the octohedral configuration of 6-co-ordinate compounds of those elements. The evidence so gained may be summarized in the following table.

Table 2

Compounds resolved for $\text{M}^n =$

$[\text{M}^n(\text{C}_2\text{O}_4)_3]\text{R}_{6-n}$	$\text{Cr}^{\text{III}}, \text{Fe}^{\text{III}}, \text{Co}^{\text{III}}, \text{Al}^{\text{III}}, \text{Rh}^{\text{III}}, \text{Ir}^{\text{III}}, \text{Pt}^{\text{IV}}$
$[\text{M}^n \text{en}_3]\text{X}_n$	$\text{Co}^{\text{III}}, \text{Pt}^{\text{IV}}, \text{Cr}^{\text{III}}, \text{Rh}^{\text{III}}, \text{Ir}^{\text{III}}, \text{Zn}^{\text{II}}, \text{Cd}^{\text{II}}$
$[\text{M dipyr} \text{dyl}_3]\text{X}_2$	$\text{Fe}^{\text{II}}, \text{Ni}^{\text{II}}, \text{Ru}^{\text{II}}$



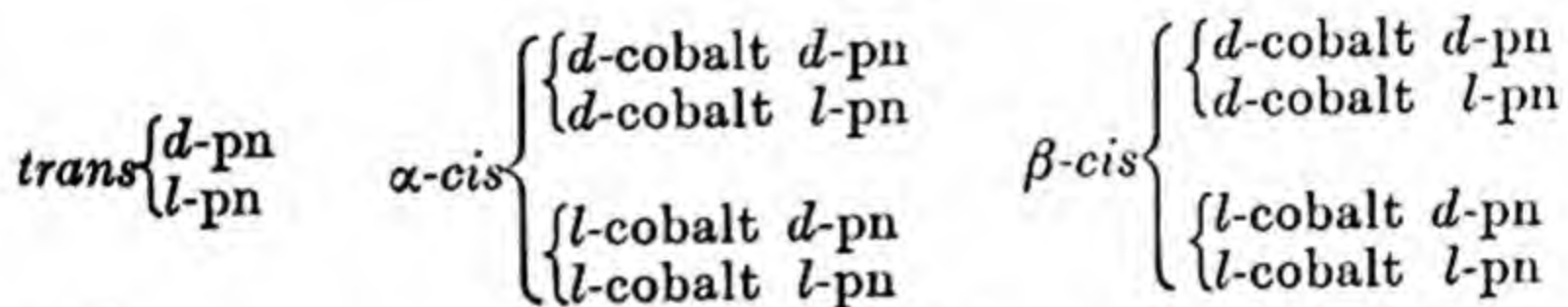
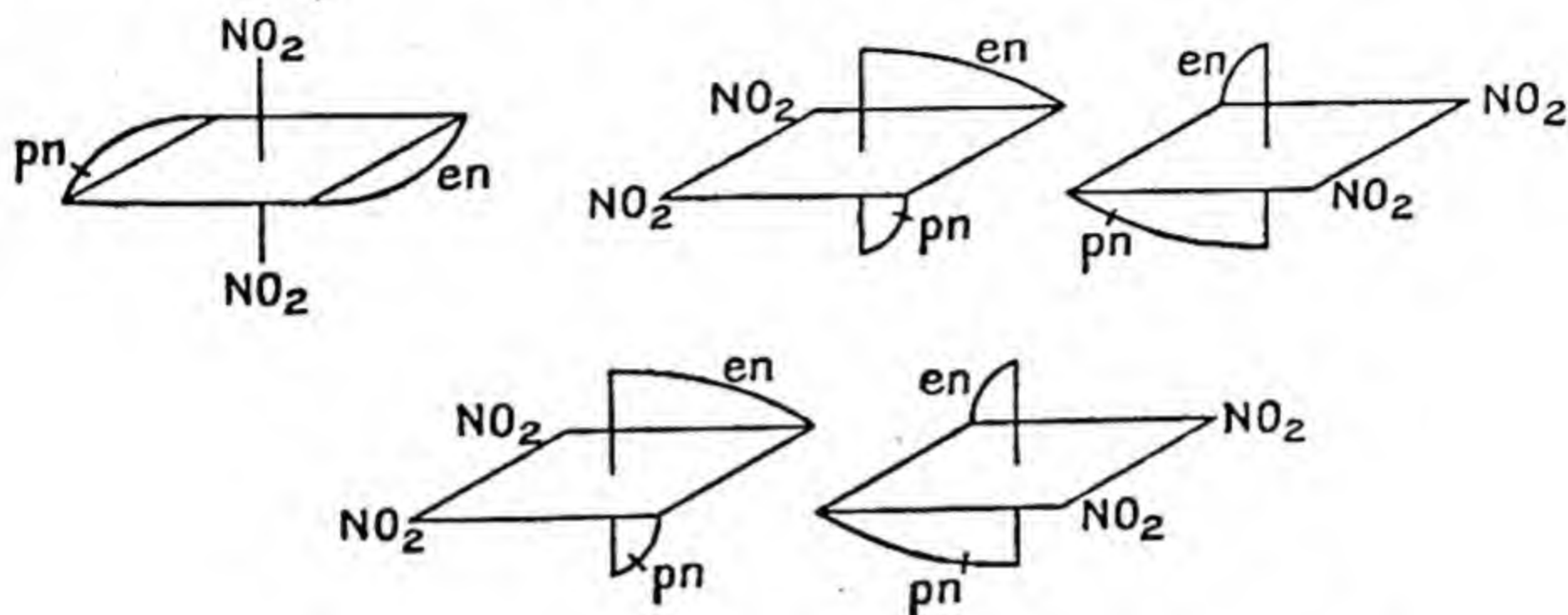
In addition, numerous compounds of the type $[\text{M en}_2\text{AB}]$ have been resolved, especially compounds of cobalt and iridium. Of this type also is the compound $[\text{Ru}(\text{C}_2\text{O}_4)_2(\text{C}_5\text{H}_5\text{N})(\text{NO})]\text{K}$, the resolution of which establishes the octohedral configuration of 6-co-ordinate ruthenium.

Where an existing asymmetric centre is introduced into a complex, the possibilities of isomerism are greatly increased, and cases arise which have no counterpart in the stereochemistry of carbon. One such case, fully investigated by Werner,¹⁰ is that of the salt

⁹ Werner, *ibid.*, 1912, 45, 121.

¹⁰ Werner, *Helv. Chim. Acta*, 1918, 1, 5.

$[\text{Co en pn}(\text{NO}_2)_2]\text{Br}$, where the symbol pn stands for propylene diamine, $\text{NH}_2\text{CH}_2\dot{\text{C}}\text{H}(\text{CH}_3).\text{NH}_2$. Since this itself contains an asymmetric carbon atom (*), it may enter into combination either in its *d* or its *l* form. The *trans* complex, itself not asymmetric, may then be formed either with *d*- or with *l*-pn, while two distinct series of the *cis* isomers should exist:



All the predicted active isomers, partial racemates and complete racemates could be isolated.

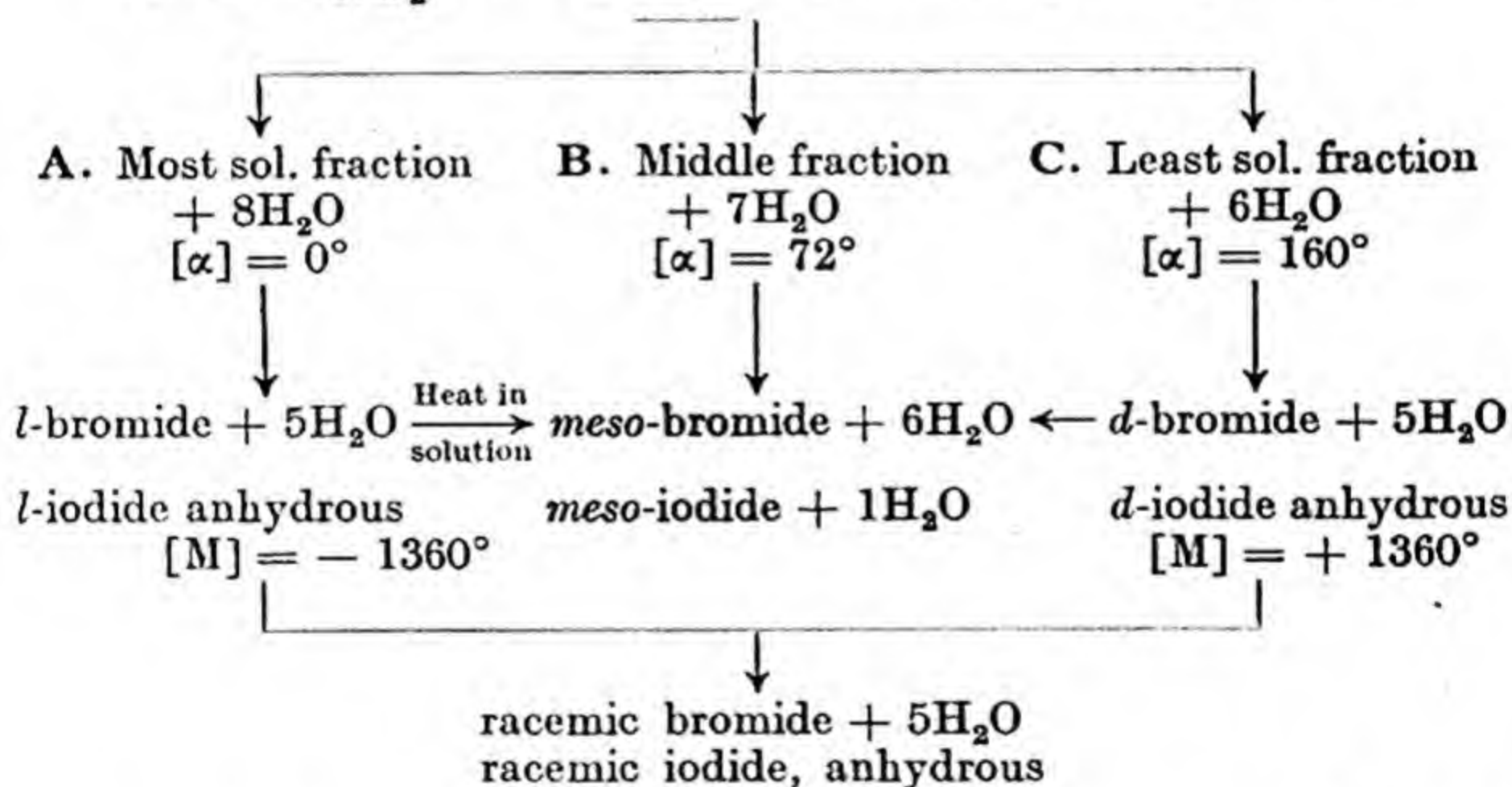
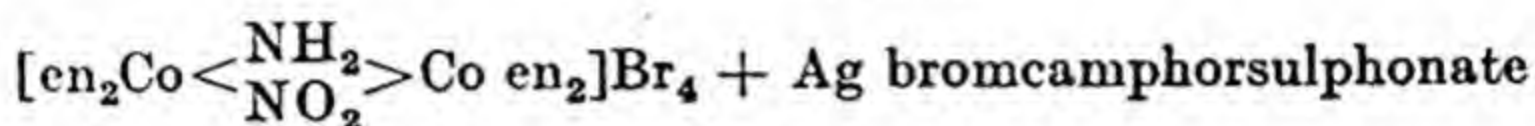
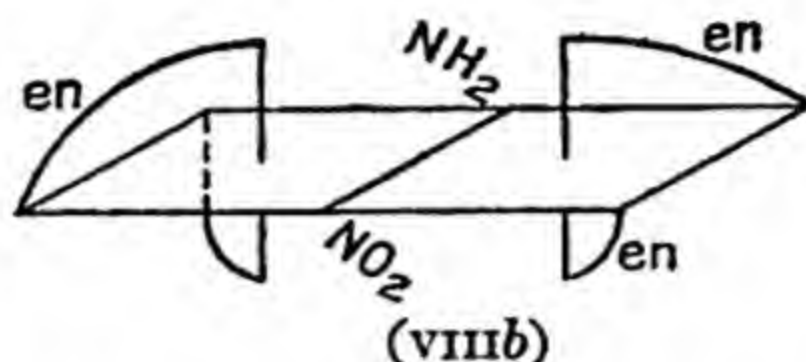
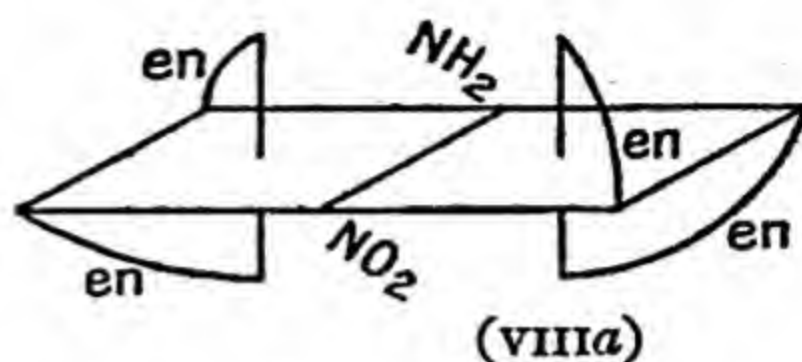
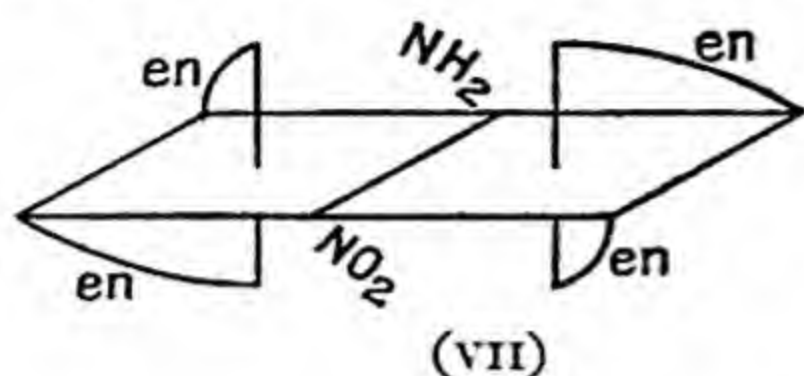
In binuclear complexes (see above, p. 113, and also p. 150) it is possible to have two asymmetric centres in the molecule. If, moreover, the asymmetric centres are structurally similar, there should exist an internally compensated or *meso* form, in addition to the dextro- and lævorotatory isomers. The case is analogous to that of tartaric acid amongst the active carbon compounds. This prediction of his theory Werner realized experimentally¹¹ in

the resolution of $\left[\text{en}_2\text{Co} \begin{array}{c} \text{NH}_2 \\ \diagup \quad \diagdown \\ \text{NO}_2 \end{array} \text{Co en}_2 \right] \text{X}_4$. The bromide of this

complex, on treatment with silver *d*-bromcamphorsulphonate, yielded the corresponding bromcamphorsulphonate, which could be separated into three fractions of differing solubility. The middle fraction proved to be the bromcamphorsulphonate of the inactive *meso* complex (VII). In confirmation of this, the solubility and degree of hydration of the salts of the *meso* isomer differ conclusively

¹¹ Werner, *Ber.*, 1913, 46, 3674.

from those of the racemate made from equimolecular quantities of the *d*- and *l*-forms (VIIIa and b).



Purely Inorganic Optically Active Compounds.—In all the cases considered hitherto, optical activity has been exhibited by complexes containing co-ordinated carbon compounds—ethylenediamine, oxalate radicals, etc. While the complete fulfilment of predictions based upon the octohedral hypothesis can now leave no doubt at all as to the steric arrangement of the co-ordinated complex, and as to the origin of the molecular dissymmetry, it nevertheless was logically desirable to prepare optically active compounds of purely inorganic nature. Only two such compounds have yet been resolved—the first, by Werner, in 1914, and the second, by F. G. Mann, in 1933.

The resolution effected by Werner¹² was that of the hexol dodecammine tetracobaltic ion, $\left[\text{Co} \begin{array}{c} \text{HO} \\ \diagup \quad \diagdown \\ \text{HO} \end{array} \text{Co}(\text{NH}_3)_4 \right]_3^{6+}$. The

polynuclear compounds of this series, which are obtained by the action of ammonia on the chloroaquatetrammine cobaltic salts $\left[\text{Co}(\text{NH}_3)_4 \begin{array}{c} \text{H}_2\text{O} \\ \text{Cl} \end{array} \right] \text{X}_2$, are in principle the analogues of the triethylene-

diamine cobaltic salts $[\text{Co en}_3] \text{X}_3$. The heavy $\left[(\text{NH}_3)_4 \text{Co} \begin{array}{c} \text{OH} \\ \diagup \quad \diagdown \\ \text{OH} \end{array} \right]$

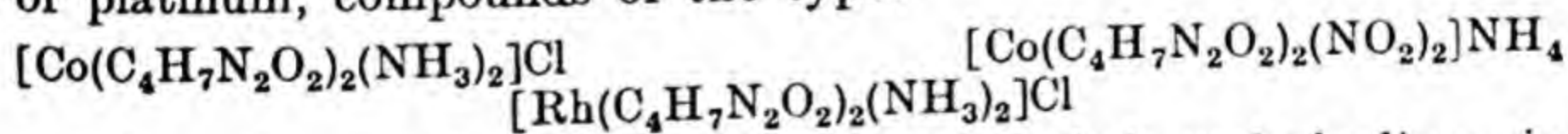
groups simply function as chelating groups about the central cobalt atom. The compound was resolved by means of brom-camphorsulphonic acid, and gave *d* and *l* forms of great optical stability with the very high rotation of $[\text{M}]_D = \pm 47,600^\circ$.

Mann's compound belongs to the general type $[\text{M en}_2 \text{AB}]$, and offers some features of special interest. Mann¹³ has pointed out that chelating groups fall into two classes:

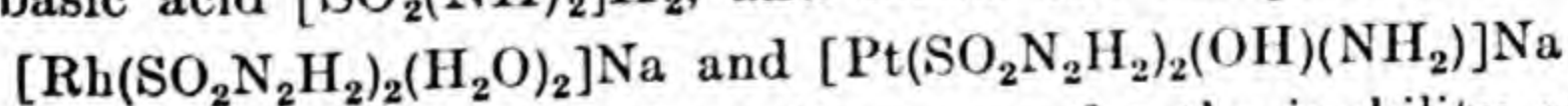
- (a) those that can fill all six co-ordination positions, as can ethylenediamine or the oxalate radical;
- (b) those which, while capable of filling four positions in the 4-co-ordinate complex, cannot fill more than four co-ordination positions when introduced into the 6-co-ordinate complex.

To this type belongs, *e.g.*, dimethylglyoxime.

Tschugaieff¹⁴ has shown that although dimethylglyoxime fills completely the four co-ordination positions about nickel, palladium or platinum, compounds of the types



are formed with the 6-co-ordinate metals cobalt and rhodium, in which it occupies four co-ordination positions. Mann showed that sulphamide, $\text{SO}_2(\text{NH}_2)_2$, acts as a chelating group of the second type. It co-ordinates with rhodium and platinum, functioning as a dibasic acid $[\text{SO}_2(\text{NH})_2]\text{H}_2$, and forms the complex salts



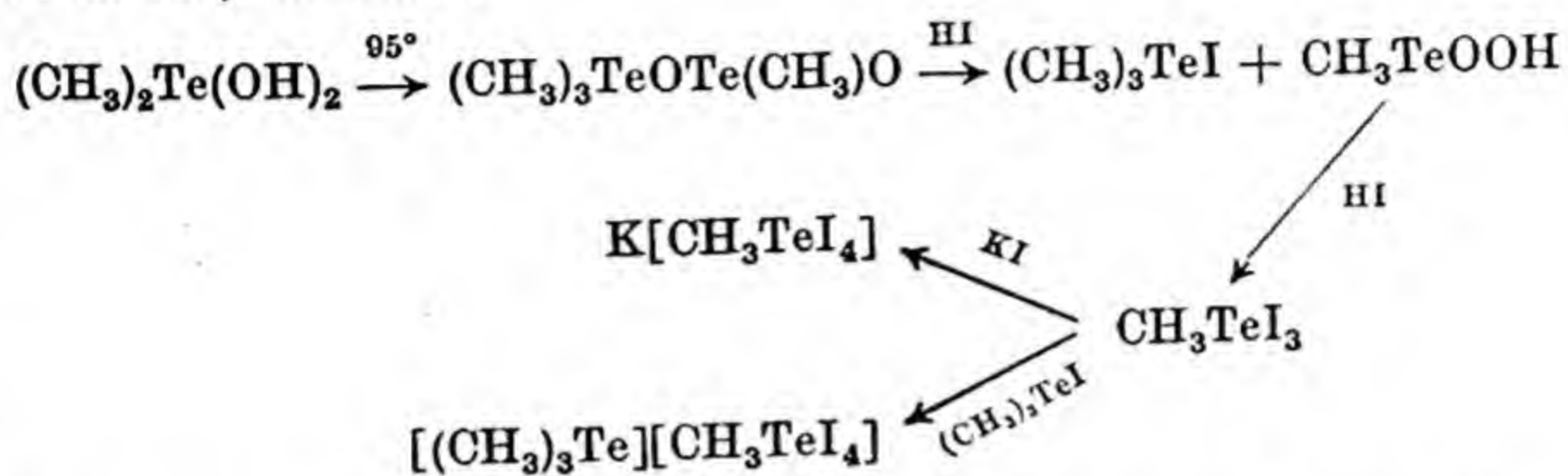
It might well be expected that the reason for the inability of the chelating group to fill all six co-ordination positions lay in the preponderating stability of the *trans* compound (IX). This is not dissymmetric, and could not be resolvable into optical isomers.

¹² *Ber.*, 1914, 47, 3087.

¹³ *J.C.S.*, 1933, 412.

¹⁴ *Z. anorg. Chem.*, 1905, 46, 144; *Ber.*, 1906, 39, 2692; 1907, 40, 3498; 1908, 41, 2226.

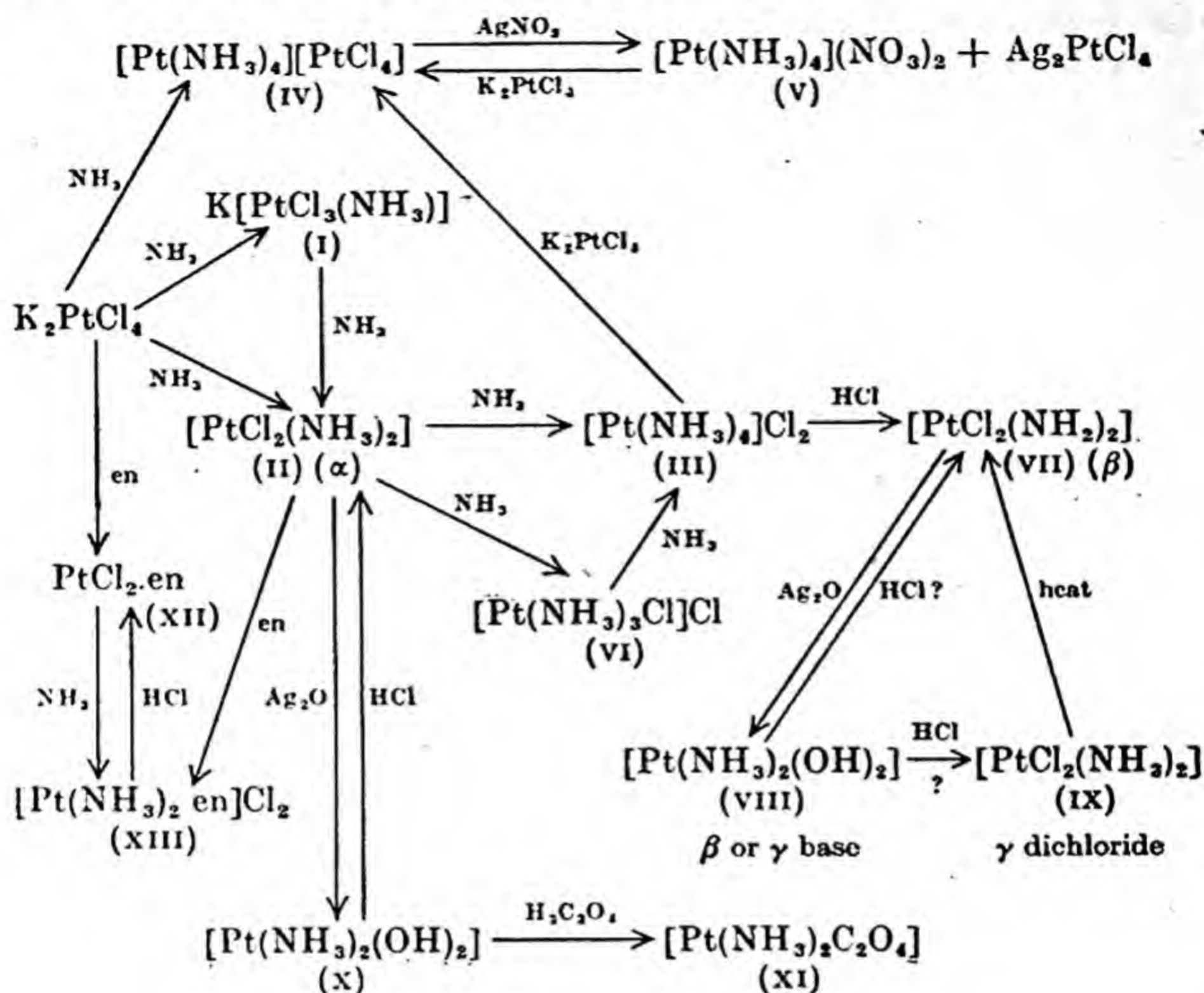
the β -base and β -diiodide are dimeric, the latter being a salt or a double compound $(\text{CH}_3)_3\text{TeI} \cdot \text{CH}_3\text{TeI}_3$. The dimeric β -base reacts with a limited amount of hydriodic acid to give a mixture of $(\text{CH}_3)_3\text{TeI}$ and $\text{CH}_3\text{TeO} \cdot \text{OH}$, both of which may be isolated. The latter compound in turn, with hydriodic acid, forms methyl telluronium triiodide CH_3TeI_3 , which unites with potassium iodide to give a double salt, or with trimethyl telluronium iodide to re-form Vernon's β -diiodide :



It is certain that the distribution of groups about 4-co-ordinate tellurium is actually tetrahedral.

The Stereochemistry of Platinum.—The principal chemical evidence as to the relations between the platinous ammines is set out in the table below. By the action of ammonia on potassium or ammonium chlorplatinite there are formed directly three compounds: a green, insoluble, highly characteristic compound, known as Magnus' salt (IV); a soluble potassium or ammonium amminotrichlorplatinite (I), usually known as Cossa's salt; and a yellow, insoluble crystalline compound (II) having the same empirical formula as Magnus' salt, which is α -diammine platinous chloride. This dissolves in an excess of ammonia, forming tetrammine platinous chloride (III); by the regulated action of ammonia—*e.g.* by boiling (II) with potassium cyanate, which liberates ammonia slowly by hydrolysis—the intermediate compound (VI), chlorotriammine platinous chloride, may be isolated. The nature of these compounds, and the transition from the tetracido compounds to the tetrammine salts, by way of the non-electrolyte, diammine platinous chloride, is shown by the equivalent conductivity of the salts in solution:

K_2PtCl_4	$\Lambda = 268$	3 ions
$\text{K}[\text{PtCl}_3(\text{NH}_3)]$	107	2 ions
$(\beta) \text{PtCl}_2(\text{NH}_3)_2$	1.2	un-ionized
(α)	22	
$[\text{Pt}(\text{NH}_3)_3\text{Cl}]\text{Cl}$	116	2 ions
$[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$	261	3 ions



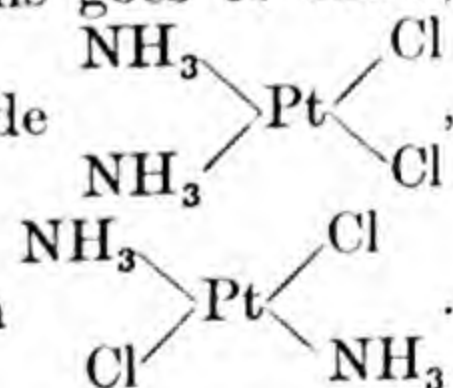
The constitution of Magnus' salt (IV) is shown in that it is produced quantitatively by the interaction of equimolecular amounts of tetrammine platinous chloride (III) and potassium chlorplatinate. In confirmation of this, and showing that no intramolecular changes occur in the reaction, when (IV) is rubbed up with silver nitrate, silver chlorplatinate is formed, and (V) is formed in solution, as is shown by its reconversion to (IV) on further treatment with potassium chlorplatinate. Tetrammine platinous chloride (III) loses 2 molecules of ammonia when it is boiled with hydrochloric acid. The α -diammine (II) is not re-formed thereby, but a second compound (VII) of the same empirical formula is produced, with a much lower solubility, and with different physical and chemical properties, known as β -diammine platinous chloride. The nomenclature of these compounds is confusing and inconsistent: the α -diammine has been variously known as Peyrone's chloride, platosemidiammine chloride and the α -diammine chloride; the β -diammine has been called Reiset's chloride, platosammine chloride and the β -diammine chloride. The nomenclature used here is that generally current in

the literature of chemistry,¹⁷ although Drew, Wardlaw and their co-workers¹⁸ reversed the designations of the diammine chlorides and their derivatives.

On the view that the α - and β -diammines are related as *cis-trans* isomers, the allocation of their configurations follows simply from their reactions. The α -diammine reacts with silver oxide to give a base (X) from which, by the action of oxalic acid, an α -diammine oxalate (XI) is formed. The β -chloride (VII) similarly reacts with silver oxide to form a second base (VIII). Whereas, however, the action of hydrochloric acid on the α -base (X) re-forms the original α -chloride (II), the base (VIII), according to Drew, Wardlaw *et al.*,¹⁸ gives rise to a new, unstable γ -chloride (IX), which is readily reconverted to the β -chloride (VII). The existence of the γ -chloride has been denied by other workers,¹⁹ and its physical and chemical properties are not convincingly distinct from those of the α -chloride. If its existence be real, it cannot easily be reconciled with the planar distribution of the co-ordinated groups, which admits of only two geometrical isomers unless arbitrary hypotheses are introduced as to the non-equivalence of adjacent bonds.

By the action of ethylenediamine on potassium chlorplatinite, a diammine compound (XII) is formed, which reacts with ammonia to give a mixed tetrammine (XIII) identical with that obtained by the action of ethylenediamine on the α -diammine chloride (II). As compared with these reactions, the β -chloride (VII) will not react with ethylenediamine, neither does the β (or γ) base (VIII) react with oxalic acid. The evidence of these reactions goes to show,

therefore, that the α -diammine is the *cis* chloride



whereas the β -compound has the *trans* configuration

Additional weight is lent to this identification of stereoisomers by the observation of Pinkard, Saenger and Wardlaw²⁰ that ethylenediamine does, indeed, react with mixed β -diammines—*e.g.* with β -[Pt(NH₃)(NH₂OH)Cl₂]⁺—but that the reaction occurs only with the complete elimination of the groups originally co-ordinated with the platinum, forming [Pt en₂]Cl₂.

Geometrical isomerism similar to that shown by the amines is found also with other platinum compounds of the type PtCl₂X₂,

¹⁷ Cf. K. A. Jensen, *Z. anorg. Chem.*, 1935, 225, 123; D. P. Mellor, *Chem. Reviews*, 1943, 33, 137.

¹⁸ *J.C.S.*, 1932, 988.

¹⁹ Cf. Rosenblatt and Schleece, *Ber.*, 1933, 66, 472; K. A. Jensen, *Z. anorg. Chem.*, 1936, 229, 252.

²⁰ *J.C.S.*, 1933, 1056.

notably the thioether compounds or sulphines, $(R_2S)_2PtCl_2$.²¹ The agreement of the chemical evidence as to the configuration of the sulphines with that adduced for the amines is of particular importance, inasmuch as two independent lines of physical evidence can be invoked as to the configuration of these compounds.

The evidence of X-ray determinations of crystal structure supports not only the hypothesis of a planar arrangement of the valencies, but also the allocation of configurations deduced from the chemical evidence considered. Thus, Dickinson²² found the halogen atoms and the platinum atom in K_2PtCl_4 to be rigidly coplanar; a similar arrangement of the ammonia molecules has been shown by Cox²³ to hold good for $[Pt(NH_3)_4]Cl_2$. While this is true for these symmetrical complex ions, in the solid state at least, it could not logically be inferred that a planar structure is valid also for all substituted complexes. Cox, Saenger and Wardlaw²⁴ have shown, however, from X-ray considerations, that the molecule of the β -disulphine must possess a plane of symmetry perpendicular to a twofold axis of symmetry—a requirement compatible only with a *trans*-planar arrangement of the groups. This accords completely with the chemical deductions for the β -series. A similar confirmation for the α -series is lacking, although the same authors have shown that the molecular symmetry is lower than in the case of the β -sulphines.

A second line of physical evidence as to the configuration of the platinous complexes is afforded by measurements of their dipole moments. Jensen²⁵ found that the β -tertiary phosphine and arsine derivatives, $(R_3As)_2PtCl_2$ and $(R_3P)_2PtCl_2$, have no dipole moment. This can only be true if each pair of Pt—Cl, Pt—As or Pt—P links is strictly collinear—i.e. if the complex is, once again, *trans*-planar in configuration. As would be expected, the α -compounds have high dipole moments. The reason for choosing the tertiary phosphine and arsine compounds for the purpose, instead of the sulphines, is that the AsR_3 or PR_3 group (R = ethyl, butyl, etc.), being pyramidal, has its resultant moment along the direction of the co-ordinate link. The resultant moment of the SR_2 group in the sulphines must be at an angle to the co-ordinate link, and if—as is most likely—there is free rotation about the co-ordinate

²¹ Blomstrand, *J. prakt. Chem.*, 1888, 38, 352; Tschugaev, *Z. anorg. Chem.*, 1913, 82, 420; Drew, Wardlaw *et al.*, *J.C.S.*, 1933, 1294; Cox, Wardlaw *et al.*, *ibid.*, 1934, 182; Jensen, *Z. anorg. Chem.*, 1935, 225, 97, 115; Drew and Wyatt, *J.C.S.*, 1934, 56.

²² *J. Amer. Chem. Soc.*, 1922, 44, 774, 2404.

²³ *J.C.S.*, 1932, 1912; *cf. also ibid.*, 1932, 2527; 1933, 1089.

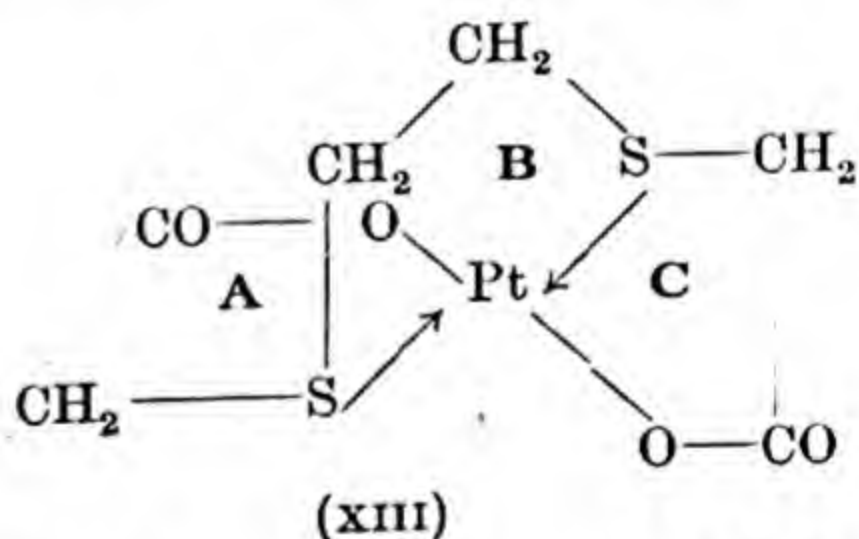
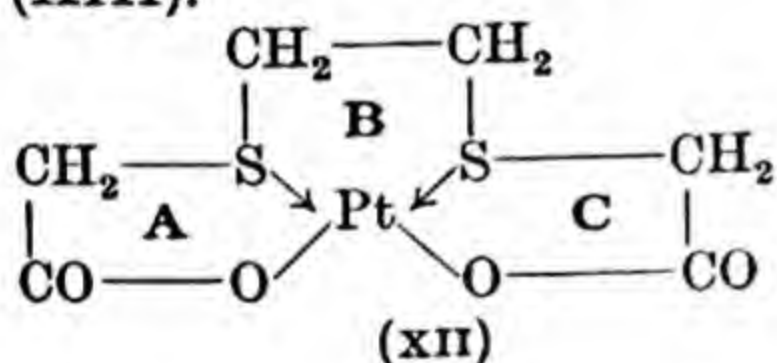
²⁴ *Ibid.*, 1934, 1012.

²⁵ *Z. anorg. Chem.*, 1936, 229, 225.

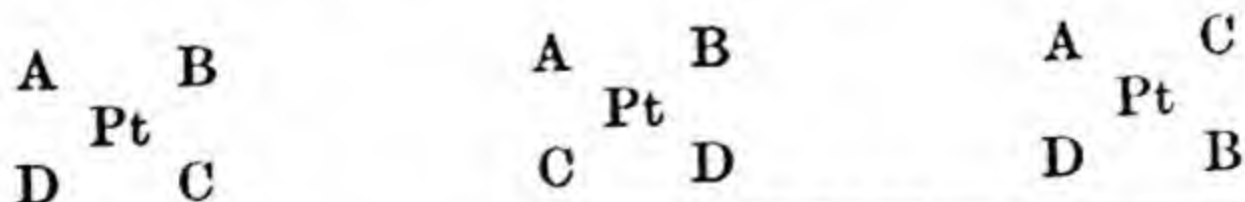
link, the whole complex will probably have a resultant moment, even though the groups are *trans*-planar in arrangement; a parallel is found in the resultant dipole moment of quinol dimethyl ether, *p*-CH₃O.C₆H₄.OCH₃.

It may be seen that the evidence as to the β or *trans* compounds of platinum is fairly complete. The case of the α isomers is not so conclusive, and it has been maintained by some that their properties differ sufficiently from those of the β -series to justify regarding them as structural, rather than geometrical, isomers. It must, however, be borne in mind that the proximity of the negative atoms in such compounds might well be sufficient by itself to account for their considerably greater chemical reactivity and electrolytic conductivity.

The view that, contrary to Werner's hypothesis, the configuration of platinous complexes is tetrahedral, and not planar, or else that both tetrahedral and planar forms are possible, has been persistently maintained by some chemists, and the evidence which finally establishes the planar configuration may now be examined. Thus, Reihlen²⁶ has maintained that in the platinous compound of ethylene bis-thioglycollic ether, prepared by Ramberg and Tiberg, a coplanar arrangement of the two coupled chelate rings (XII) would impose a great strain in the median ring B, which can be avoided only if the two rings A and C are at right angles, as is the case if the platinum valencies are tetrahedrally disposed (XIII).



A very elegant method of verifying the planar configuration of the platinous complex, reminiscent of the method applied by Ladenburg to the benzene problem, was worked out by Tscherniaev.²⁷ In any planar complex [Pt ABCD] containing four different substituents, there should be three isomeric arrangements of the co-ordinated groups:

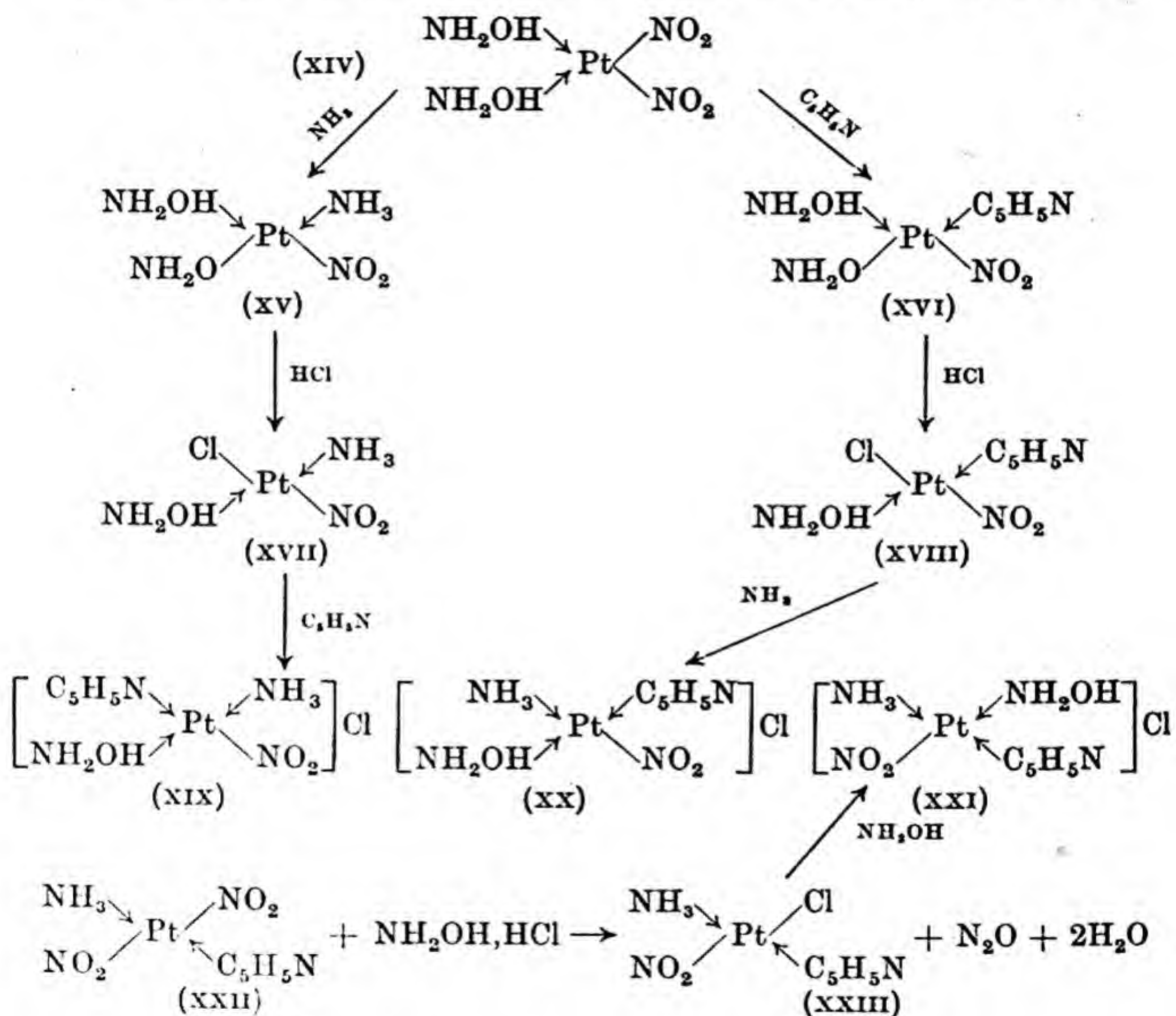


²⁶ *Annalen*, 1926, 448, 312; 1931, 489, 42.

²⁷ *Ann. Inst. Platine*, 1928, 6, 55; *Chem. Zentr.*, 1929, i, 1204.

In a tetrahedral structure, of course, only one arrangement is possible.

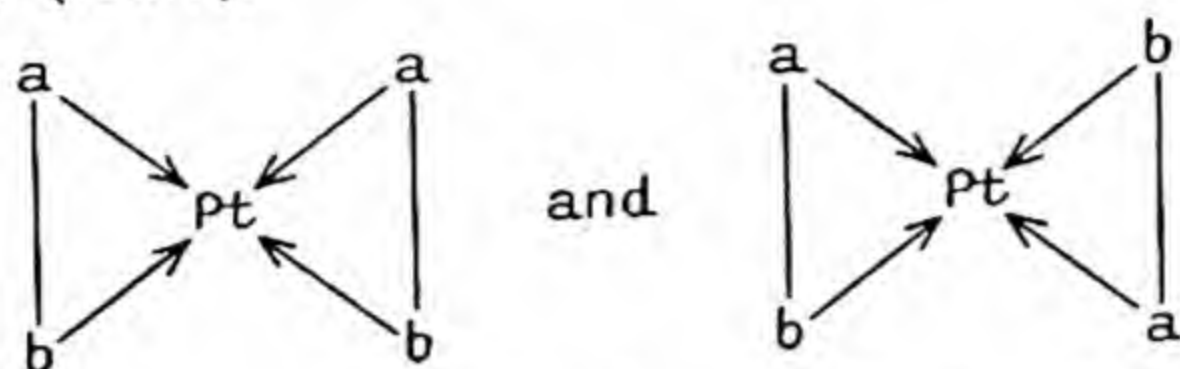
Tscherniaev, starting from the *cis*-dihydroxylamino platinous nitrite (XIV), obtained the diammine compounds (XV) and (XVI) by the action of ammonia and pyridine. These compounds, when treated successively with hydrochloric acid and pyridine, respectively, were converted to the diammines (XVII) and (XVIII), and then to the isomeric triammines (XIX) and (XX). The third



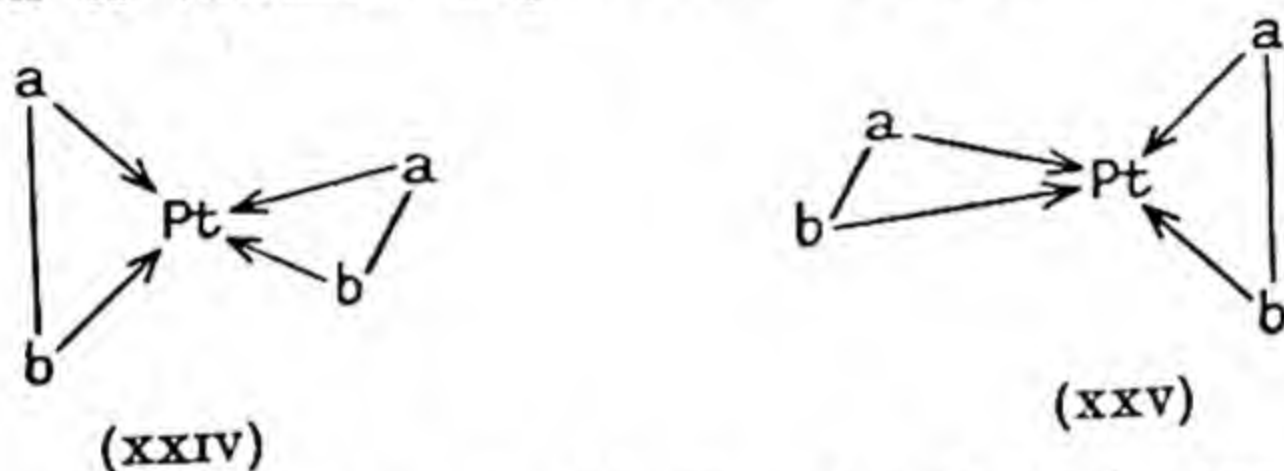
isomeride (XXI) was obtained from *trans*-amminopyridino platinous chloride (XXII). One of the nitrito groups reacts with hydroxylamine hydrochloride, whereby a chloride ion is introduced into the complex (XXIII). The compound (XXIII) is converted into the desired third isomeride (XXI), by the action of hydroxylamine.

Attempts to settle the question have been made by utilizing the possibilities of optical activity which may arise from the introduc-

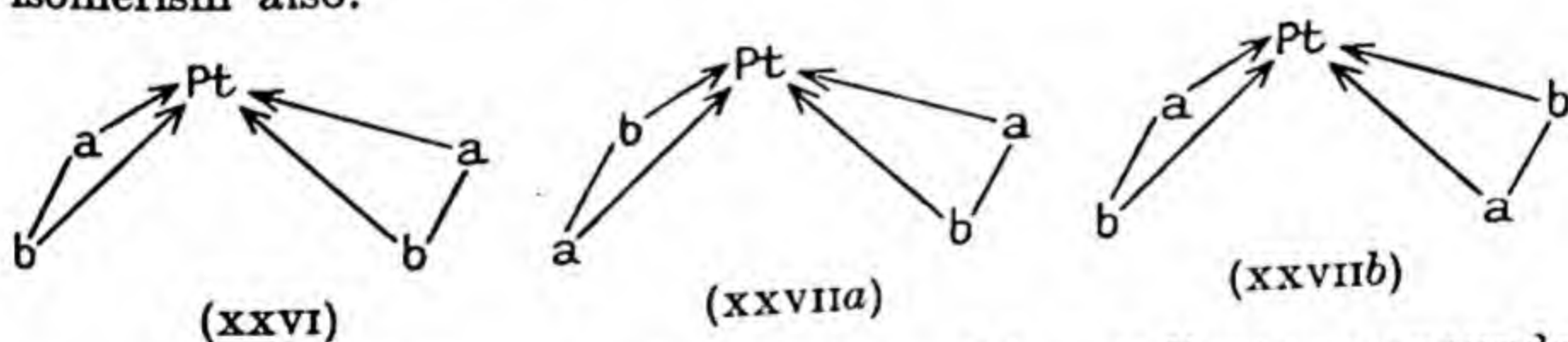
tion of unsymmetrical chelating groups. Then, on a planar model, complexes of the type $[\text{Pt}(a-b)_2]$, where $a-b$ is the unsymmetrical chelating group, must exist in two forms, neither of which is resolvable, which are related to one another as *cis-trans* isomers. On the tetrahedral model, no geometrical isomerism is possible, but the complex should be resolvable into optical enantiomorphs (XXIV) and (XXV).



A third possibility, intrinsically less likely, is that a pyramidal distribution of valencies might exist. Two geometrical isomers,



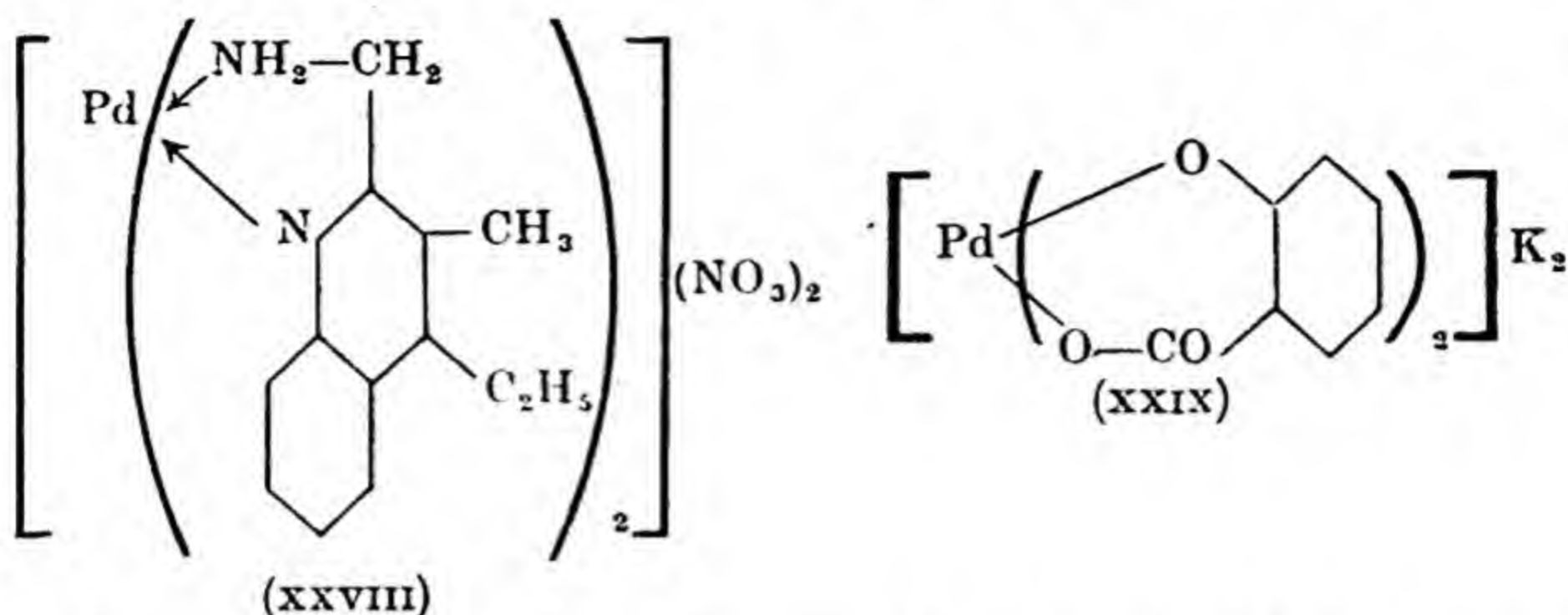
(XXVI) and (XXVII), should then be formed, one of which (corresponding to the planar *trans* form) should display optical isomerism also.



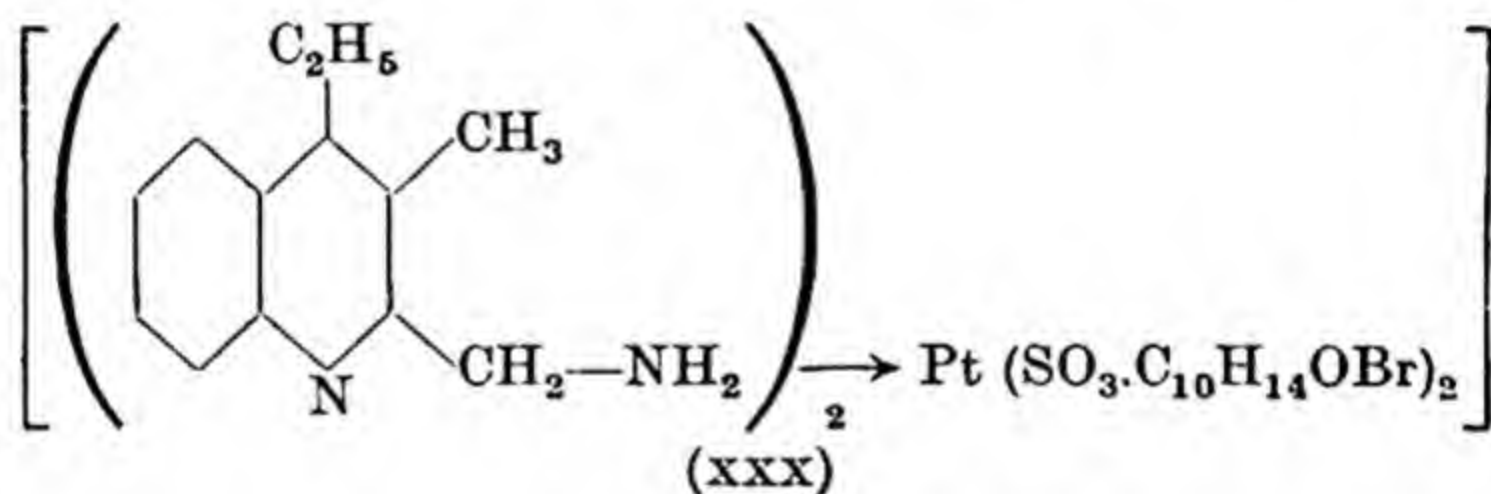
Several cases of the alleged resolution of 4-co-ordinate compounds of the platinum metals have, indeed, been reported. Reihlen²⁸ claimed to have resolved the bromcamphorsulphonate of the series (XXVIII), although no active salt of an inactive acid could be obtained. A similar claim was made by Rosenheim and Gerb²⁹ for the salicylato-palladite anion (XXIX). The low optical stability of such compounds is noteworthy, however, and in the face of the other evidence available, they cannot be regarded as indicating any possibility of a tetrahedral configuration.

²⁸ *Annalen*, 1931, 489, 42; 1935, 519, 80; 1935, 520, 256.

²⁹ *Z. anorg. Chem.*, 1933, 210, 289.



Jensen,³⁰ who tried without success to extend Reihlen's observations, has suggested that the anomalous rotation of the bromocamphorsulphonate solutions could be explained if the chelate rings of (XXVIII) open, forming (XXX) in solution. This last compound is, of course, destroyed when the resolved bromocamphorsulphonate is later converted to the salt of an inactive acid.



Drew,³¹ using isobutylenediamine, $\text{NH}_2\text{CH}_2\text{C}(\text{CH}_3)_2\text{NH}_2$, as the unsymmetrical chelating group, found that the predicted geometrical isomers of $[\text{Pt}(a-b)_2]\text{X}_2$ could be prepared. It is significant that both isomers were non-resolvable. If one of the molecules $a-b$ be now replaced by two different unfunctional groups, c and d , then the following possibilities arise for the configuration of the resulting

complex $\left[\begin{smallmatrix} a \\ b \end{smallmatrix} \text{Pt}(c)(d) \right]$:

- (a) If both planar and tetrahedral forms exist, there must be two isomers, whether the chelating group is unsymmetrical, as with isobutylenediamine, or symmetrical, as with ethylenediamine.
- (b) If the configuration is planar, there is only one compound if

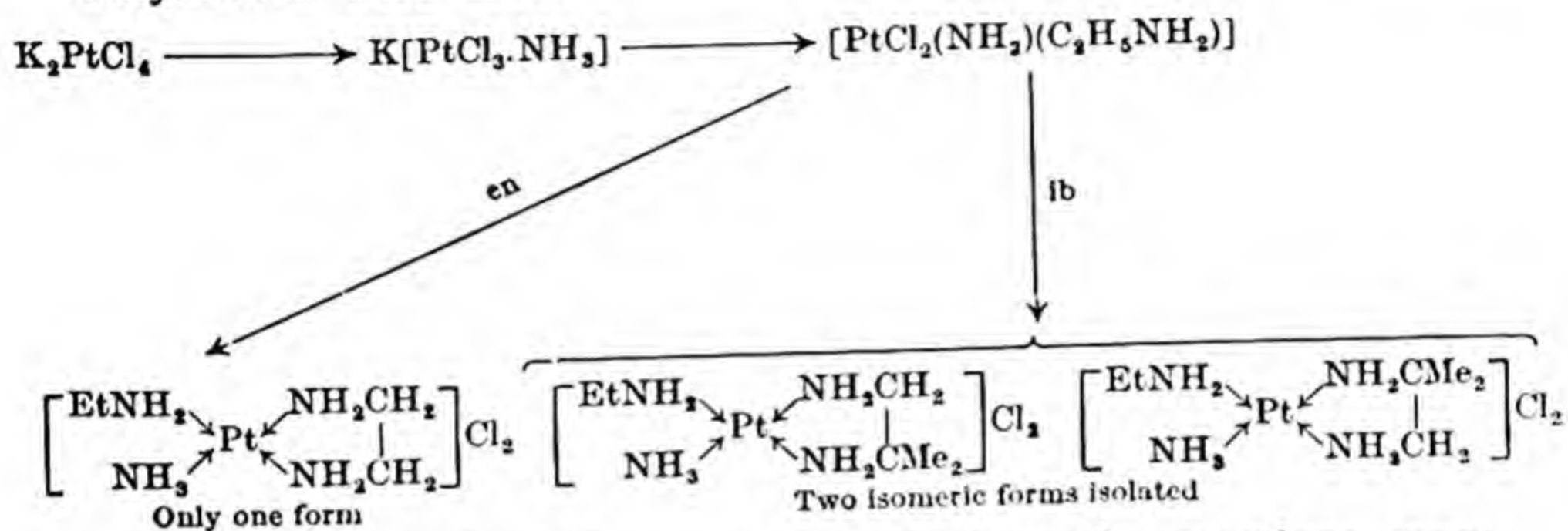
³⁰ *Z. anorg. Chem.*, 1938, **241**, 115.

³¹ *J.C.S.*, 1934, 221; *ibid.*, 1937, 1549.

$a-b$ is symmetrical, but two isomers if $a-b$ is unsymmetrical. In no case are the compounds resolvable.³¹

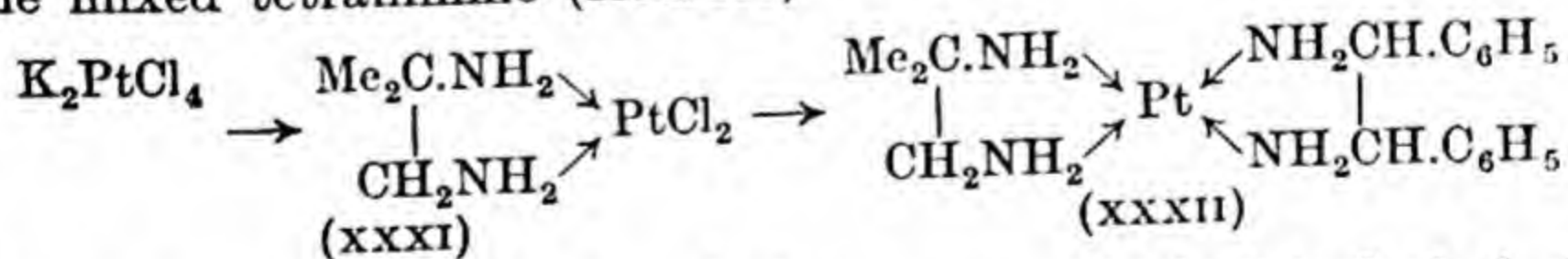
- (c) If the configuration is tetrahedral, there is only one form, which is resolvable if $a-b$ is unsymmetrical, but not resolvable if $a-b$ is symmetrical.

As chelating groups, Drew used isobutylenediamine and ethylenediamine; as the unfunctional groups c and d , ammonia and ethylamine were used.



The experimental evidence, summarized in the reactions represented above, accords entirely with the hypothesis that only the planar arrangement is possible.

Finally, Mills and Quibell³² have furnished positive evidence by resolving a bis-chelate compound which could not exhibit mirror-image isomerism if the chelate rings were in planes perpendicular to one another. Isobutylenediamine reacts with potassium chlorplatinate, forming isobutylenediamine platinous chloride (XXXI), from which, by the action of *meso*-stilbene diamine, there is obtained the mixed tetrammine (XXXII)

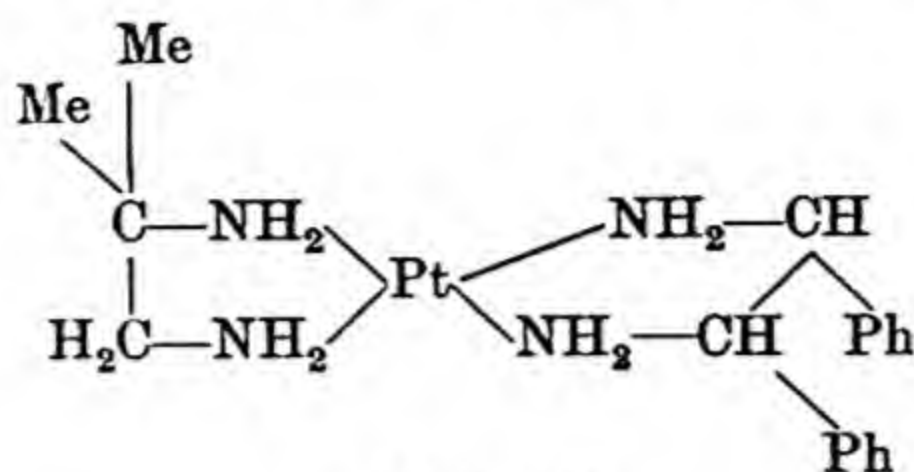


If the arrangement of the platinum valencies is tetrahedral, the tetrammine must have the molecular configuration which is shown diagrammatically in perspective and end elevation in (XXXIII) and (XXXIV) respectively. This has, as may be seen, a median plane of symmetry, and so cannot give rise to optical isomerism. If the two chelate rings are coplanar, however, the molecule is dissymmetric, as may be seen from (XXXV) and (XXXVI).

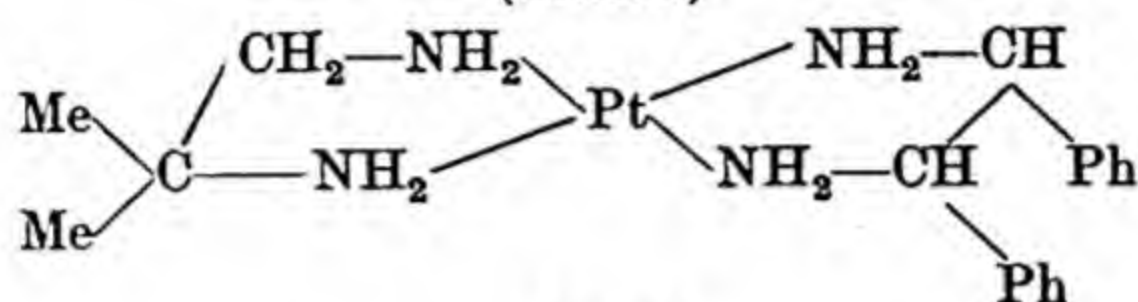
The tetrammine was resolved by Mills and Quibell into stable enantiomorphs, having $[\alpha]_{\text{D}}^{25} = \pm 48.5^\circ$. Since simple complexes such

³² *Ibid.*, 1935, 839.

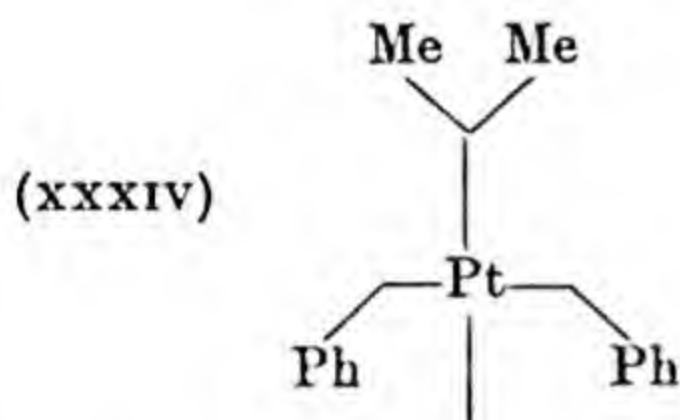
as $[\text{Pt en ib}]\text{Cl}_2$ (ib = isobutylene diamine) have never been resolved, there is no evidence in favour of the inherently improbable



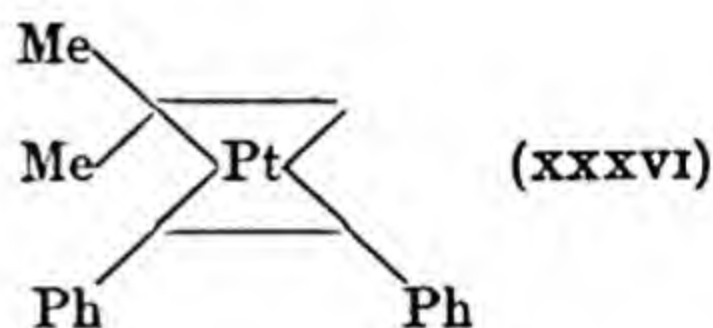
(xxxiii)



(xxxv)



(xxxiv)



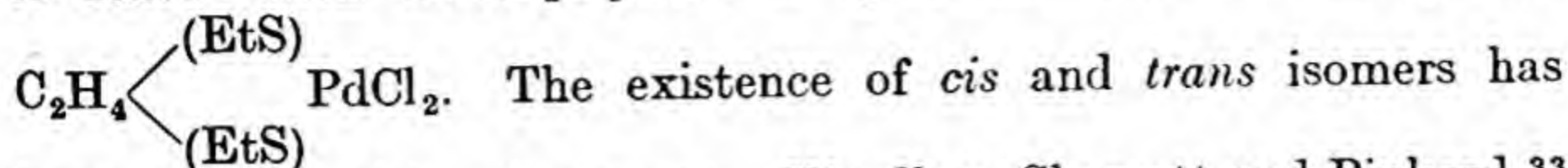
(xxxvi)

pyramidal configuration. The planar distribution of groups around the central atom in the complex compounds of divalent platinum may therefore be taken as conclusively established.

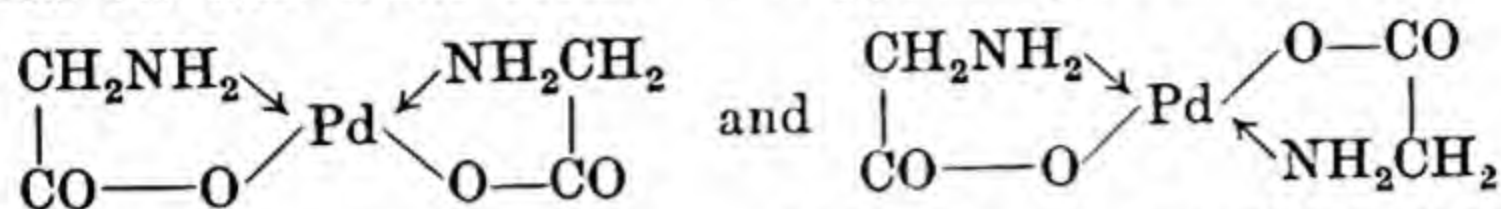
The Stereochemistry of Other 4-Co-ordinate Elements.

Palladium.—It might well be expected, from the chemical similarity between platinum and palladium, that the latter element would also have a planar arrangement of valencies. This is, indeed, the case. The general reactions of palladous compounds with ammonia and with thioethers conform closely to those described for platinum, although in most cases only one of the possible pairs of isomers is formed, namely—except with chelate groups—the β or *trans* isomer, as is shown by the reactions of the compounds, and by the isomorphism of $(\text{Et}_2\text{S})_2\text{PdCl}_2$ with $\beta\text{-(Et}_2\text{S)}_2\text{PtCl}_2$. The study of the palladous compounds is complicated, however, by the ease with which intramolecular rearrangement takes place. Thus, $(\text{NH}_3)_2\text{PdCl}_2$, although undoubtedly a *trans* compound, reacts readily with potassium oxalate, forming $[(\text{NH}_3)_2\text{PdC}_2\text{O}_4]$, which is necessarily *cis*. In the same way, as has been stated, $(\text{Et}_2\text{S})_2\text{PdCl}_2$ is isomorphous with $\beta\text{-(Et}_2\text{S)}_2\text{PtCl}_2$, but

it reacts with $\text{EtS.C}_2\text{H}_4.\text{SEt}$ to give the chelated compound



been established in a few cases. Wardlaw, Sharratt and Pinkard³³ obtained *cis* and *trans* forms of diglycine palladium,



Mann³⁴ has prepared both *cis* and *trans* forms of $(\text{NH}_3)_2\text{Pd}(\text{NO}_2)_2$, while Grunberg and Schulmann³⁵ have recently isolated the hitherto unknown α -diammine palladous chloride, $(\text{NH}_3)_2\text{PdCl}_2$.

Nickel.—The complex chemistry of nickel, like that of palladium, bears certain resemblances to that of platinum. Thus, all three metals form characteristic inner complex salts with dialkylglyoximes, and the hydrated double cyanides—*e.g.* $\text{Ba}[\text{M}(\text{CN})_4].4\text{H}_2\text{O}$ (where $\text{M} = \text{Ni}, \text{Pd}$ or Pt)—are all isomorphous. It seems to have been first explicitly suggested by Pauling³⁶ on theoretical grounds, which will be considered later, that nickel must also be planar in the configuration of its 4-co-ordinate compounds. Tschugaieff³⁷ had already obtained two interconvertible compounds of nickel with methyl glyoxime, and Sugden,³⁸ shortly after Pauling's prediction, isolated two forms of the compound of nickel with benzylmethylglyoxime (XXXVII), also readily interconvertible, which are presumably related as *cis* and *trans* isomers. This assumption is supported by a considerable body of physical evidence. The complex dithio-

oxalates, $\text{K}_2 \left[\begin{array}{c} \text{CO.S} \searrow \\ | \\ \text{CO.S} \nearrow \end{array} \text{M} \begin{array}{c} \nwarrow \text{S.CO} \\ | \\ \text{S.CO} \end{array} \right]$, in which $\text{M} = \text{Ni}, \text{Pd}$ or Pt , are

strictly isomorphous, and Cox, Wardlaw and Webster³⁹ have shown, by X-ray methods, that the anion of the nickel compound is rigidly coplanar. The same authors⁴⁰ have also shown that the salicylaldoxime compounds (XXXVIII) are planar, *trans* structures,

The compound $[\text{NiBr}_3(\text{Et}_3\text{P})_2]$,⁴¹ containing trivalent nickel, has quite a different steric configuration. This substance appears to be correctly represented as having the unusual co-ordination number

³⁴ *Ibid.*, 1935, 1642.

³³ *J.C.S.*, 1934, 1012.

³⁵ *Compt. Rend. U.R.S.S.*, 1933, 218.

³⁶ *J. Amer. Chem. Soc.*, 1931, 53, 1367.

³⁷ *J. Russ. Phys. Chem. Soc.*, 1910, 42, 1466; *Chem. Zentr.*, 1911, i, 871.

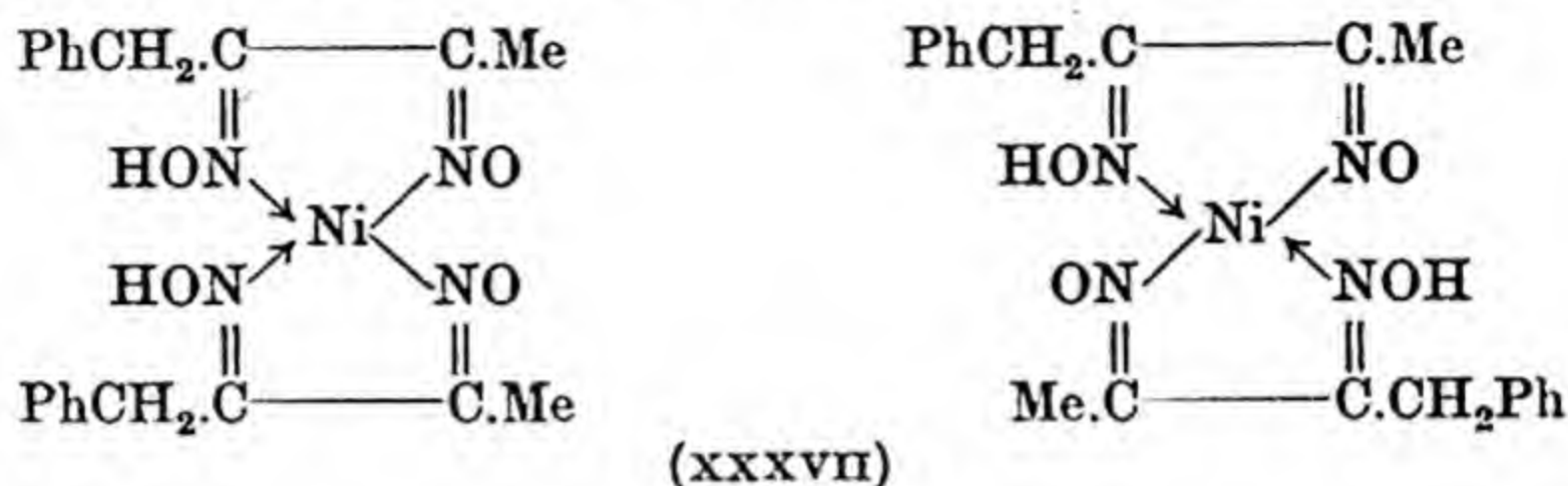
³⁸ *J.C.S.*, 1932, 246.

⁴⁰ *Ibid.*, 1935, 459.

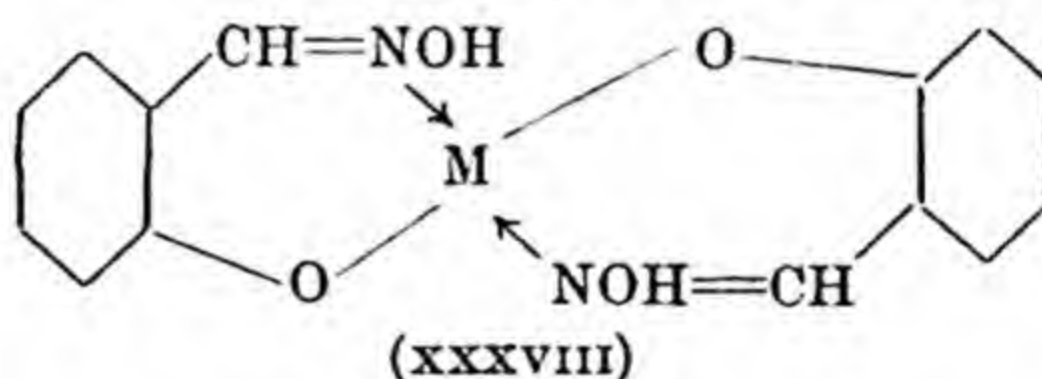
³⁹ *J.C.S.*, 1935, 1475.

⁴¹ K. A. Jensen and B. Nygaard, *Acta Chem. Scand.*, 1949, 3, 474.

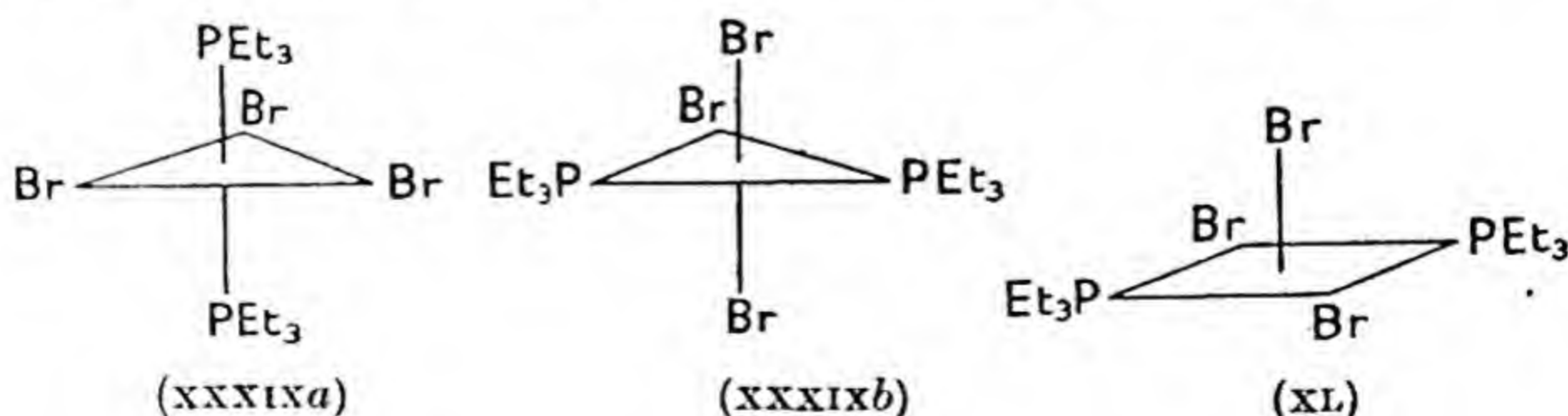
5, since its formulation as a binuclear complex (*q.v.*) containing both Ni (ii) and Ni (iv) cannot be reconciled with the molecular weight in organic solvents. Moreover, its magnetic susceptibility indicates the presence of one unpaired electron, as would be expected in any complex based on trivalent nickel (*see p. 181*). There are two likely configurations for a molecule of this kind: the trigonal bipyramid (XXXIX), or the tetragonal pyramid (XL). It is known that the dipole moment of the $\text{Et}_3\text{P} \rightarrow \text{Metal}$ bond is large, so that the



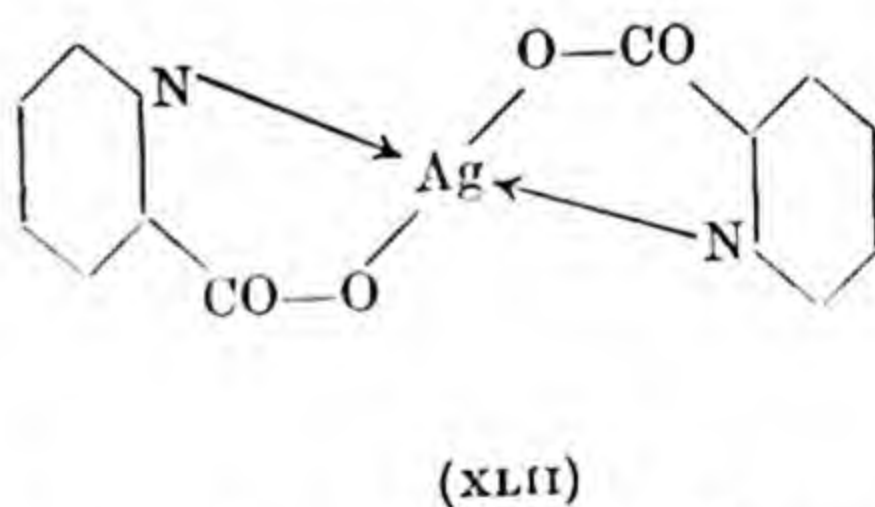
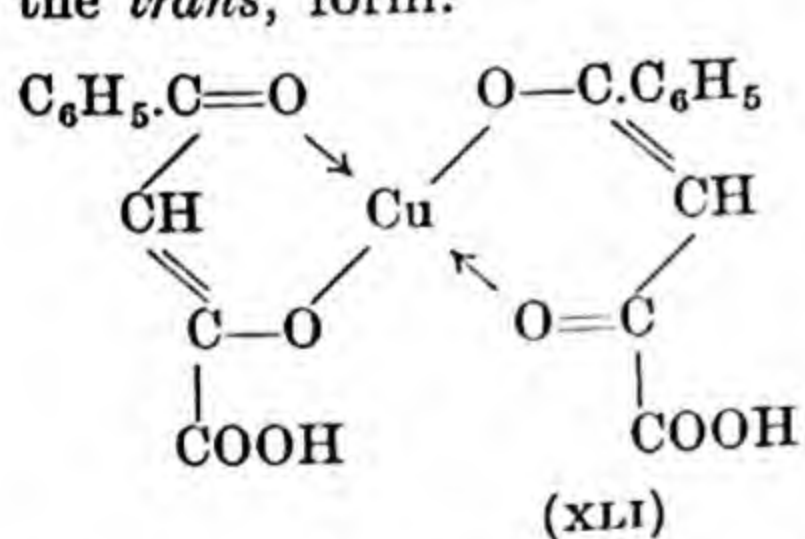
α -form, m.p. 168° .
 β -form, m.p. $75\text{--}77^\circ$.



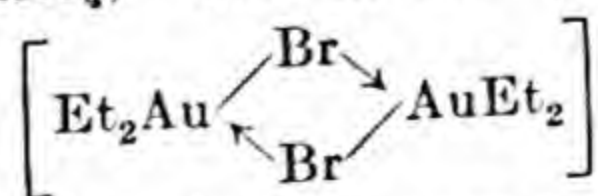
possible arrangements of the groups about the structure (XXXIX) necessarily all lead to large moments or to zero moment. As the dipole moment found for $[\text{NiBr}_3(\text{Et}_3\text{P})_2]$ is small, but not zero, Jensen and Nygaard believe that the configuration of the 5-coordinate complex is to be represented by (XL), and that the structure assigned to some other $[\text{AB}_5]$ molecules—*e.g.* to $\text{Fe}(\text{CO})_5$ —may be in error. There are some theoretical reasons for supposing that the configuration which is taken up may depend on the quantum numbers of the *d*, *s* and *p* orbitals which are involved (as $[dsp^3]$ or $[d^2sp^2]$ hybrids—*see Chapter III*) in forming the complex.



Copper was for some time considered to belong to those elements having a tetrahedral configuration, since Mills and Gotts ⁴² obtained a strychnine salt of cupribenzoyl pyruvic acid (XLI) which exhibited the phenomenon of mutarotation. They were not able to remove the strychnine without complete racemization, but by analogy with the behaviour of the corresponding beryllium complex, which is undoubtedly tetrahedral, and which likewise showed mutarotation, it was concluded that the copper compound had been resolved. This was possible only if the valencies were tetrahedrally disposed about the copper atom (*cf.* XXIV and XXV above). It emerged, however, from the crystal structure of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, as determined by Beevers and Lipson, ⁴³ that in the hydrated ion $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ the water molecules are coplanar with the copper atom, and it has since been shown ⁴⁴ that other cupric complexes, such as the salicylaldoxime compound and the picolinate, are also planar. It is especially noteworthy that the same holds good for inner complex salts, such as the benzoyl acetate, closely related to the compound examined by Mills and Gotts. It seems assured, therefore, that the conclusion reached by the latter authors was in error, and that copper is invariably planar in its 4-co-ordinate compounds. In no case is geometrical isomerism known amongst compounds of copper: thus, $\text{CuCl}_2(\text{C}_5\text{H}_5\text{N})_2$ exists in only one, the *trans*, form.



As might be expected, bivalent silver has the same configuration as cupric copper, as has been shown ⁴⁵ for argentic picolinate (XLII). The same planar form of the complex is found also for trivalent gold in KAuBr_4 , ⁴⁶ and in diethylauric bromide,



The planar configuration thus appears to be the normal for the platinum-nickel and copper-silver group of metals in their bivalent

⁴² *J.C.S.*, 1926, 3121.

⁴³ *Proc. Roy. Soc.*, 1934, A, 146, 570.

⁴⁴ Cox *et al.*, *J.C.S.*, 1935, 731; 1936, 775.

⁴⁵ *Idem, ibid.*, 1936, 775.

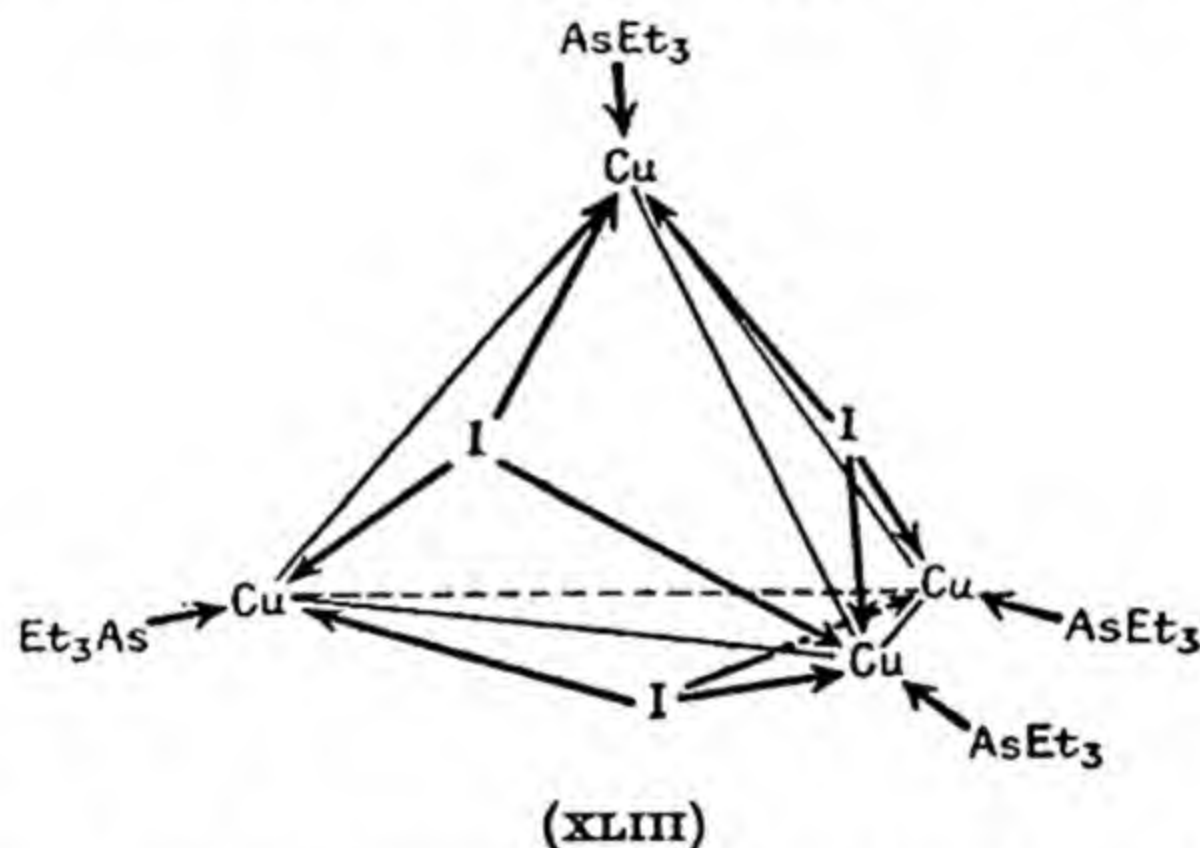
⁴⁶ Cox and Webster, *J.C.S.*, 1936, 1635.

state. It is important to note, however, that the configuration displayed depends on the valency of the metal. Thus, quadrivalent platinum in $(\text{CH}_3)_3\text{PtCl}$ ⁴⁷ is tetrahedral, as also is univalent copper

in $\left[\text{Cu} \left(\text{S}=\text{C} \begin{array}{l} \text{CH}_3 \\ \text{NH}_2 \end{array} \right)_4 \right] \text{Cl}$ and in $\text{K}_3[\text{Cu}(\text{CN})_4]$.⁴⁸ The same is

apparently true for tin and lead, which have the tetrahedral configuration in their quadrivalent compounds, but a planar configuration in the bivalent state.⁴⁹

The most interesting case, however, is that of certain cuprous compounds, such as $(\text{C}_2\text{H}_5)_3\text{As.CuI}$, in which the apparent co-ordination number is 2. Compounds of co-ordination number 2 are formed by univalent silver, and it has been shown that in $\text{K}[\text{Ag}(\text{CN})_2]$ the complex ion $[\text{Ag}(\text{CN})_2]$ is linear. The cuprous complexes are not of this type, however, but are shown ⁵⁰ by



molecular weight determinations to be fourfold polymers, $[\text{Et}_3\text{As.CuI}]_4$. The compound undergoes polymerization in order that the stable co-ordination maximum may be attained, and affords an example of the manner in which the chemistry of the metallic element is dominated by the necessity of acquiring the stable co-ordination number. In the case of these cuprous compounds, the crystal structure of the solid compounds shows that the four copper atoms are disposed at the apices of a regular tetrahedron, in such a way that each copper atom is itself surrounded tetrahedrally by three iodine atoms (each shared with two other copper atoms) and an arsine molecule (XLIII). The same tendency

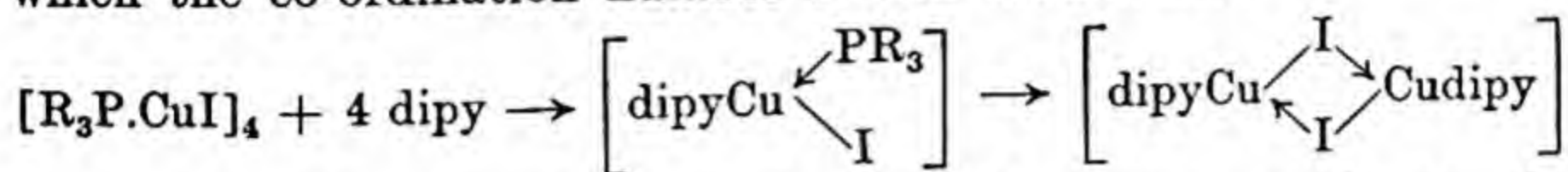
⁴⁷ *Idem*, *Z. Krist.*, A, 1935, 90, 561.

⁴⁸ Cox, Wardlaw and Webster, *J.C.S.*, 1936, 775.

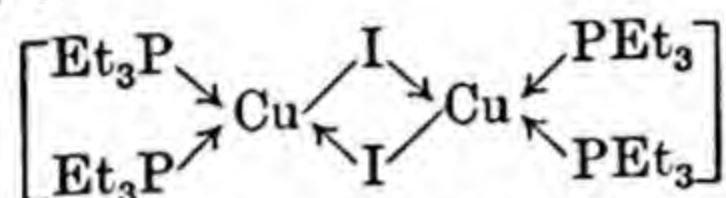
⁴⁹ Cox, Shorter and Wardlaw, *Nature*, 1937, 139, 72.

⁵⁰ Mann, Purdie and Wells, *J.C.S.*, 1936, 1503.

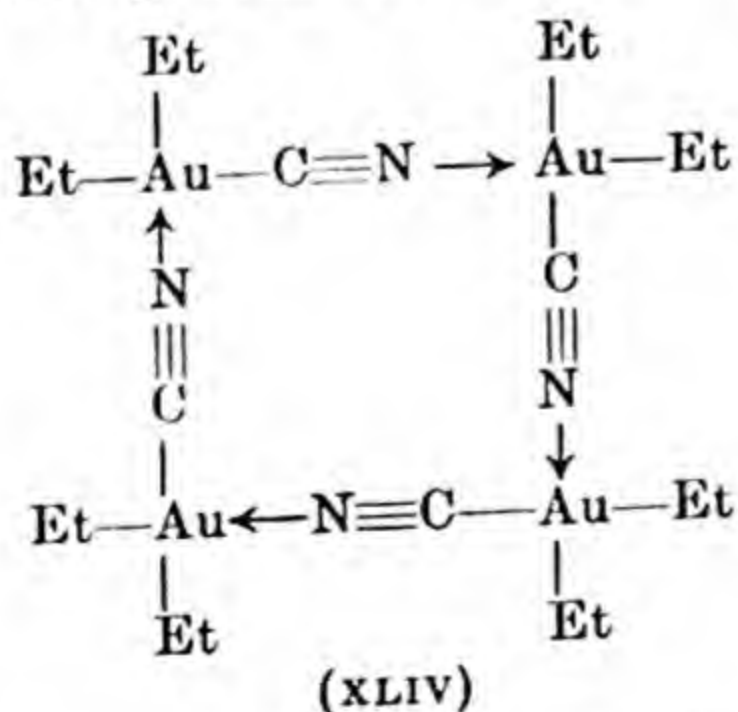
to establish fourfold co-ordination is met with in other cuprous complexes. Thus, cuprous iodide forms an ammine $[(\text{NH}_3)_3\text{CuI}]$, which loses ammonia readily (Biltz and Stollenwerk).⁵¹ Amines of greater co-ordinating power, such as dipyridyl, give stable compounds of the same type, and with the arsine and phosphine compounds already referred to, monomeric compounds with the co-ordination number four are readily formed. If these lose the alkyl phosphine component, polynuclear compounds are formed, in which the co-ordination number is still maintained.



Compounds already reported in the literature, such as the $\text{CuI} \cdot 2\text{P}(\text{C}_2\text{H}_5)_3$ described by Arbusow, are undoubtedly to be formulated similarly:



Another example of polymerization brought about by the necessity of acquiring the stable co-ordination number is afforded by diethyl cyanogold, Et_2AuCN .⁵² If this were monomeric, it would have the co-ordination number 3, and would be co-ordinatively unsaturated. Since, however, the square planar configuration is stable for trivalent gold, and since the $\text{CN}-$ group may co-ordinate with either end, the co-ordination maximum may be attained by a fourfold polymerization (XLIV). In agreement with this, the compound does, in fact, have a molecular weight in solution corresponding with the tetrameric form.



The configuration of most 4-co-ordinated elements at least, other than those indicated above, is tetrahedral. Rather surprisingly,

⁵¹ *Z. anorg. Chem.*, 1921, 119, 97.

⁵² Gibson *et al.*, *J.C.S.*, 1935, 1024.

this includes divalent cobalt, in certain of its compounds at least. Powell and Wells⁵³ have shown that in $\text{Cs}_3\text{CoCl}_5 (= \text{Cs}_2\text{CoCl}_4 + \text{CsCl})$ the cobalt is present at the centre of a tetrahedron of chlorine ions in the anion $[\text{CoCl}_4]^{2-}$. On the other hand, there is evidence⁵⁴ that in the α -, stable, violet form of $\text{CoCl}_2 \cdot (\text{C}_5\text{H}_5\text{N})_2$ the configuration must, for dimensional reasons, be planar. Dipyridinocobaltous chloride can also be obtained in an unstable, blue β -form by heating the α -form at 110° , or by crystallization from organic solvents at elevated temperatures. These two forms have been considered by some,⁵⁵ without any experimental justification, to be the *cis* and *trans* forms of planar complexes. An alternative view, that one or other of the forms is a salt $[\text{Co pyr}_4][\text{CoCl}_4]$, is difficult to reconcile with the monomeric molecular weight of the β -form in solution, with the *trans*-planar monomeric nature of the α -form, and with the observed magnetic susceptibility of the compounds.⁵⁶ The nature of the β -compound thus remains unexplained. It is clear, however, that divalent cobalt is capable of assuming both the planar and the tetrahedral configurations according to the nature of the attached groups and of the whole complex.

The evidence for the tetrahedral configuration of most of the elements is based upon the crystal structure of complex salts, such as the series $\text{K}_2[\text{M}(\text{CN})_4]$, where $\text{M} = \text{Zn}, \text{Cd}$ or Hg , or upon the optical resolution of bis-chelate compounds. Thus, Mills and Gotts⁵⁷ resolved zinc and beryllium benzoylpyruvates (see (XLI) above), and Boëseken⁵⁸ resolved disalicylato boric acid (XLV). Confirmation of the tetrahedral structure of beryllium complexes is afforded by the structure of basic beryllium acetate, $\text{Be}_4\text{O}(\text{O} \cdot \text{COCH}_3)_6$. This interesting compound, like the other so-called 'basic beryllium salts' of fatty acids, is soluble in organic solvents, melts at a low temperature, and may be distilled unchanged. They must therefore be purely covalent in structure. It has been shown⁵⁹ that in the basic acetate the beryllium atoms form a regular tetrahedron around the central oxygen atom, and are further linked by co-ordination to the six acetate groups so that each beryllium atom is itself in fourfold co-ordination (XLVI). It may be noticed that the central oxygen atom is also the centre of fourfold tetrahedral co-ordination. This is met with elsewhere also, and is concerned, as will be seen later, in the crystalline (solid) and pseudo-crystalline

⁵³ *J.C.S.*, 1935, 359.

⁵⁴ Cox, Wardlaw *et al.*, *ibid.*, 1937, 1556.

⁵⁵ *Cf.* Biltz and Fetkenheuer, *Z. anorg. Chem.*, 1914, 89, 97.

⁵⁶ Barkworth and Sugden, *Nature*, 1937, 139, 374.

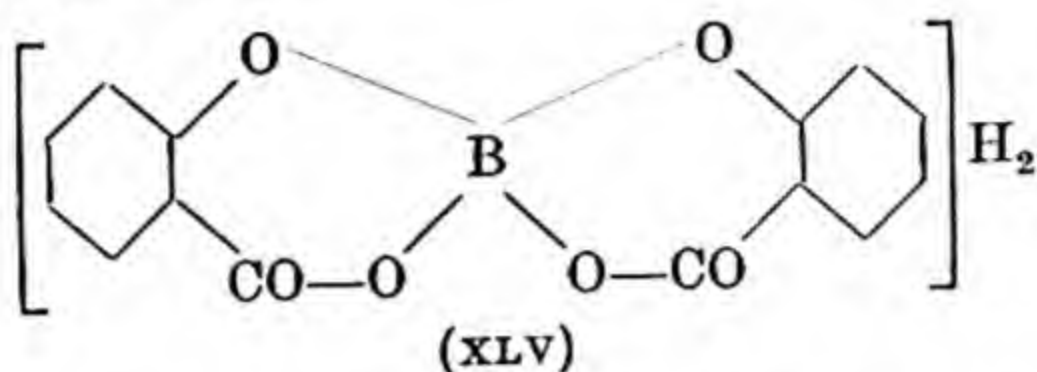
⁵⁷ *J.C.S.*, 1926, 3121.

⁵⁸ J. J. Boëseken, *Proc. Acad. Sci. Amsterdam*, 1924, 27, 174.

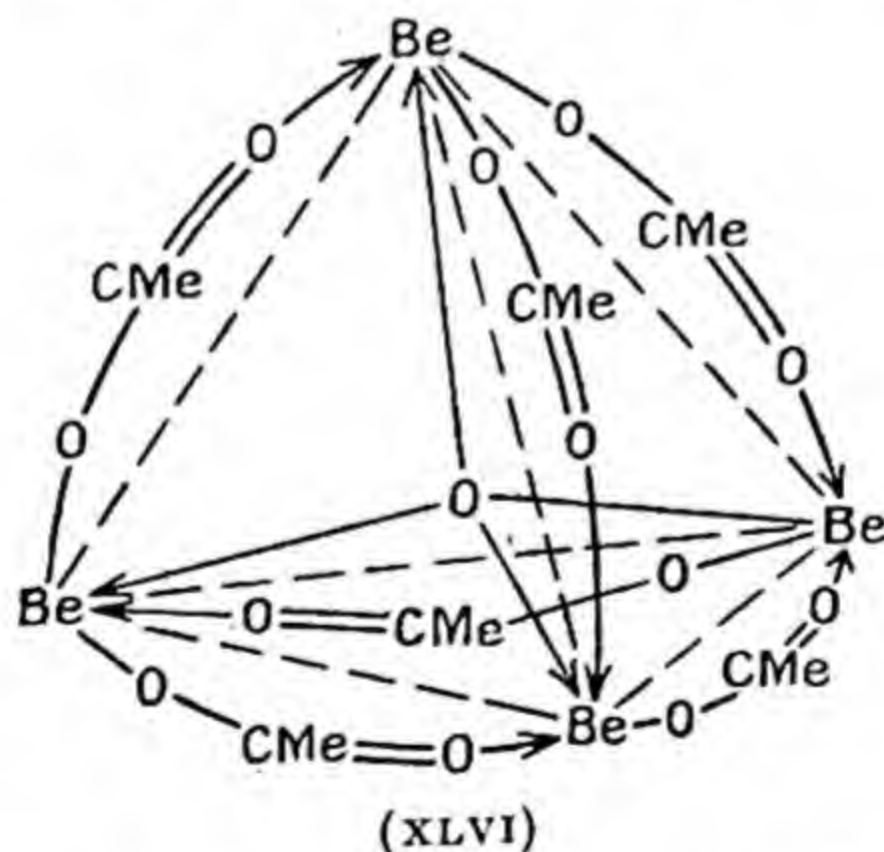
⁵⁹ W. H. Bragg and G. T. Morgan, *Proc. Roy. Soc.*, 1923, A, 104, 437.

(liquid) forms of water, and in the formation of hydroxyl bonds in hydrates and hydroxides.

The important question arises as to whether these characteristic configurations are invariable, or whether the assumption of other forms is also possible. Theoretical guidance on this point is lacking, but the experimental material appears to provide examples both of 'planar' elements forming tetrahedral complexes, and of the converse phenomenon.



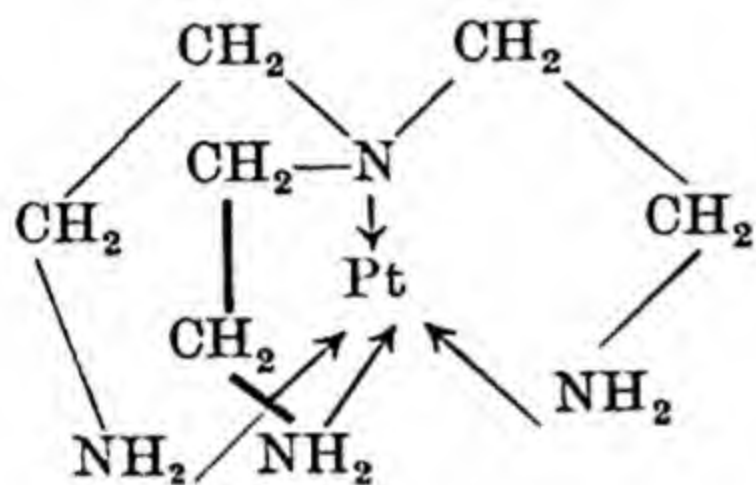
F. G. Mann⁶⁰ in 1926 investigated the formation of complex compounds by $\beta\beta'\beta''$ -triaminotriethylamine, $N(CH_2CH_2NH_2)_3$, and found that with nickel and platinous iodides this formed compounds in which it functioned as a *quadridentate group*, filling all four positions in the co-ordination shell. A problem of great interest is thereby raised, since it has been rigorously established that



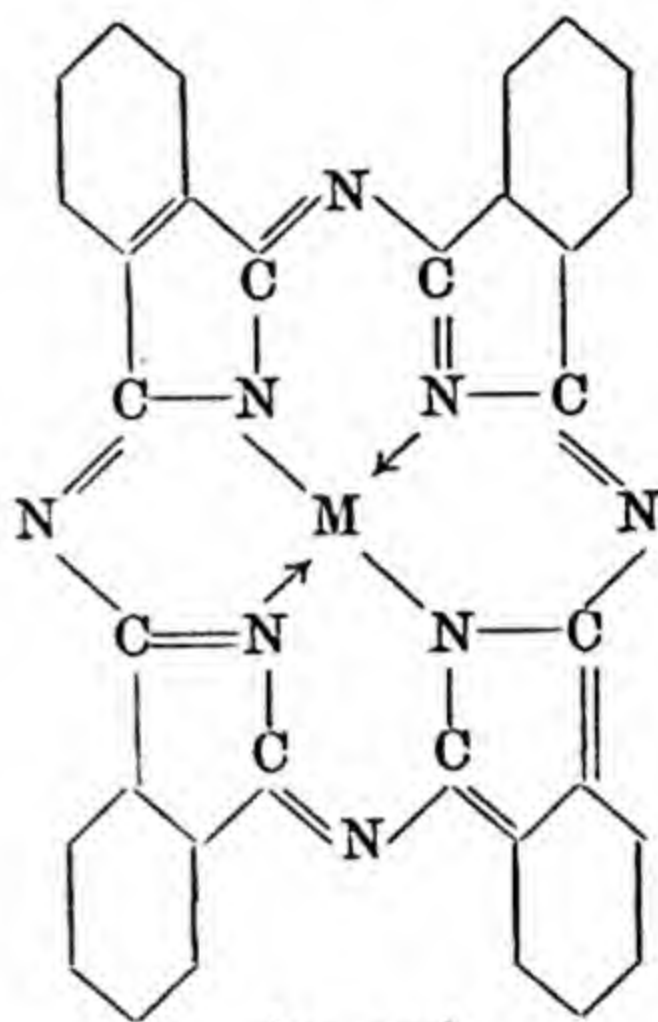
these elements normally have the planar configuration. The triaminotriethylamine, however, could not span all four positions of the square planar arrangement, although it can be fitted without undue strain to a tetrahedral structure (XLVII). It would seem, therefore, that under the constraint of groups of high co-ordinating power, the 'planar' elements may be led to take up the other structure.

⁶⁰ *J.C.S.*, 1926, 482.

The converse must hold for the phthalocyanine compounds of beryllium, zinc, magnesium, and other 'tetrahedral' elements,⁶¹ since not only is the skeleton of the molecule (XLVIII) rigidly co-planar, but the crystalline compounds have been proved by the X-ray method⁶² to possess the same structure as the phthalocyanines of nickel and copper. In some cases—*e.g.* the magnesium compound—the metal readily picks up two molecules of water or solvent, thereby going over to the 6-co-ordinate state, and stabilizing the square planar arrangement imposed by the phthalocyanine group.



(XLVII)



(XLVIII)

Ring Size and Chelation.—The manner in which chelation generally enhances the stability of co-ordination compounds will have become apparent from the preceding sections. For a molecule with two potentially co-ordinating groups—such as a diamine $\text{NH}_2(\text{CH}_2)_n\text{NH}_2$, or an amino acid $\text{NH}_2(\text{CH}_2)_n\text{COOH}$ —to function as a chelate group it must be geometrically possible to form a ring of low strain, precisely as in the formation of carbon rings in organic chemistry. Chelation will therefore be most favoured when the groups are in the 1,4 or 1,5 positions.

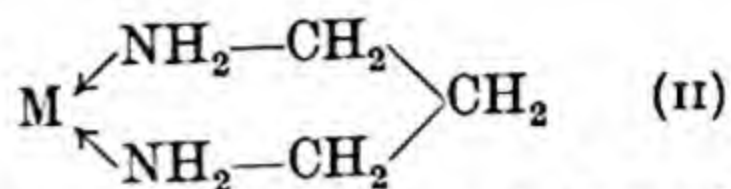
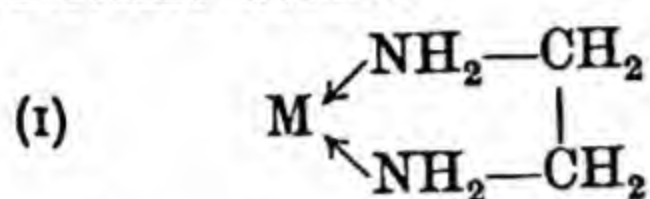
Where saturated (singly linked) rings are formed, as by the co-ordination of diamines, the 5-membered ring, as formed by ethylenediamine (I), is the most stable. Objective proof of this has been furnished by Drew,⁶³ who found that ethylenediamine

⁶¹ Linstead *et al.*, *ibid.*, 1936, 1719, and earlier papers.

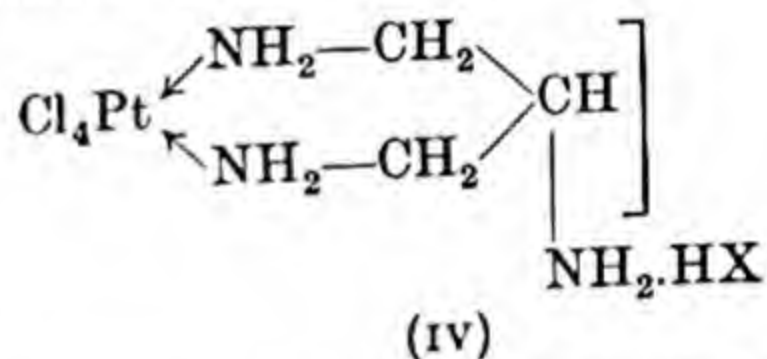
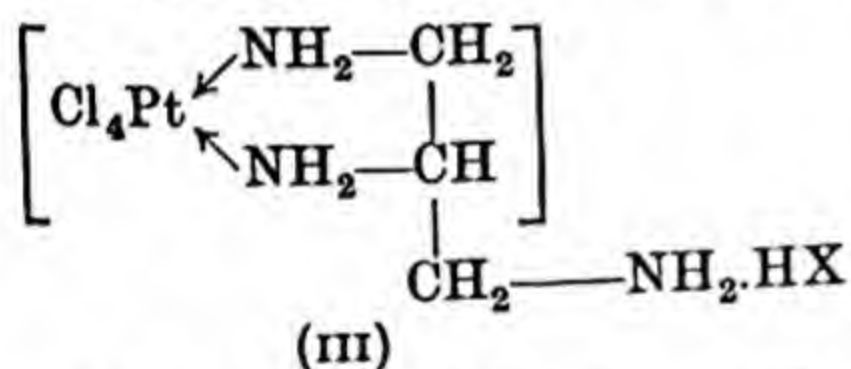
⁶² Linstead and Robertson, *ibid.*, 1936, 1736; Robertson, *ibid.*, 1935, 615; 1936, 1195.

⁶³ Drew and Tress, *J.C.S.*, 1933, 1335.

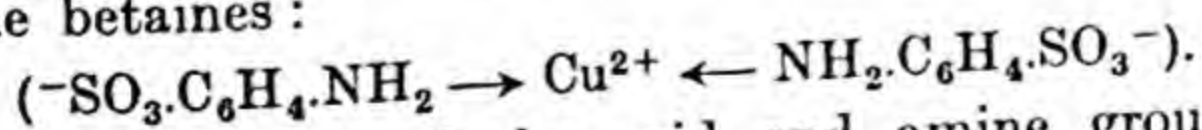
and, less readily, 1,3-propylenediamine (II), co-ordinate with platinum, whereas the higher polymethylenediamines form only amorphous, ill-defined products, in which the two amino groups of any one molecule of diamine are probably linked to different metallic atoms.



A particularly elegant demonstration of the superior stability of the five-membered as compared with the six-membered ring was given by Mann⁶⁴ in studying the co-ordination compounds of 1,2,3-triaminopropane, $\text{NH}_2\text{CH}_2\text{CH}(\text{NH}_2)\text{CH}_2\text{NH}_2$. This can react so as to occupy only two co-ordination positions, the third amine group then being capable of salt formation. The compound of this type formed with platinic chloride will then be either dissymmetric (III) or symmetrical (IV), according as a five-membered ring or a six-membered ring is formed preferentially by chelation. Mann resolved the compound into optical isomerides, thereby establishing the structure (III) with a five-membered chelate ring.



The same considerations apply to inner complex salts. Pfeiffer⁶⁵ showed that, of the amino acids $\text{NH}_2(\text{CH}_2)_n\text{COOH}$, those with $n = 1$ or 2 , giving rise to five- or six-membered rings, respectively, alone function as chelating groups. Where strong acid groups are involved, however, he has found⁶⁶ that steric considerations are overruled, complex salts of a different type being formed. Thus, the *o*-, *m*- and *p*-aminobenzene sulphonic acids all form copper salts the formula $(\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3)_2\text{Cu}\cdot 4\text{H}_2\text{O}$, which on the evidence of their colour are closely related to the simple aniline compound $(\text{C}_6\text{H}_5\text{SO}_3)_2\text{Cu}(\text{NH}_2\text{C}_6\text{H}_5)_2$. Plainly, in these cases co-ordination is effected only by the amine group, giving a structure analogous to that of the betaines:



The steric relationship of the acid and amine groups is then irrelevant.

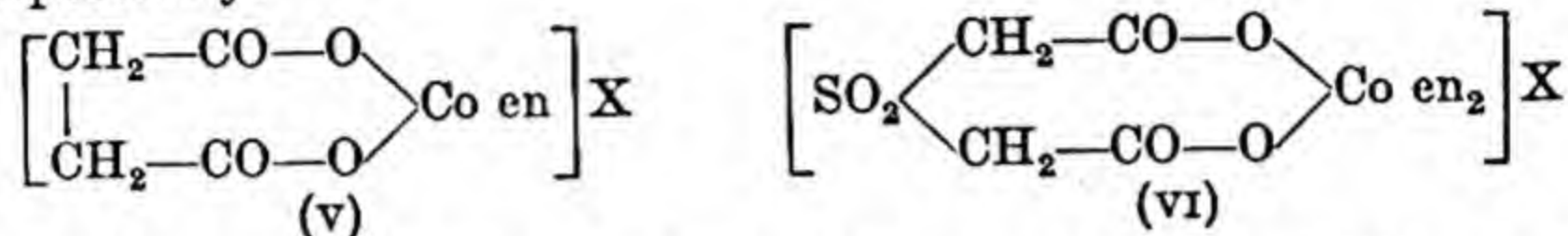
⁶⁴ *J.C.S.*, 1926, 129, 2681.

⁶⁵ *Annalen*, 1933, 503, 84; *J. pr. Chem.*, 1933, [ii], 136, 321.

⁶⁶ Pfeiffer, *Z. anorg. Chem.*, 1936, 230, 97; cf. Ley, *Ber.*, 1924, 57, 1700.

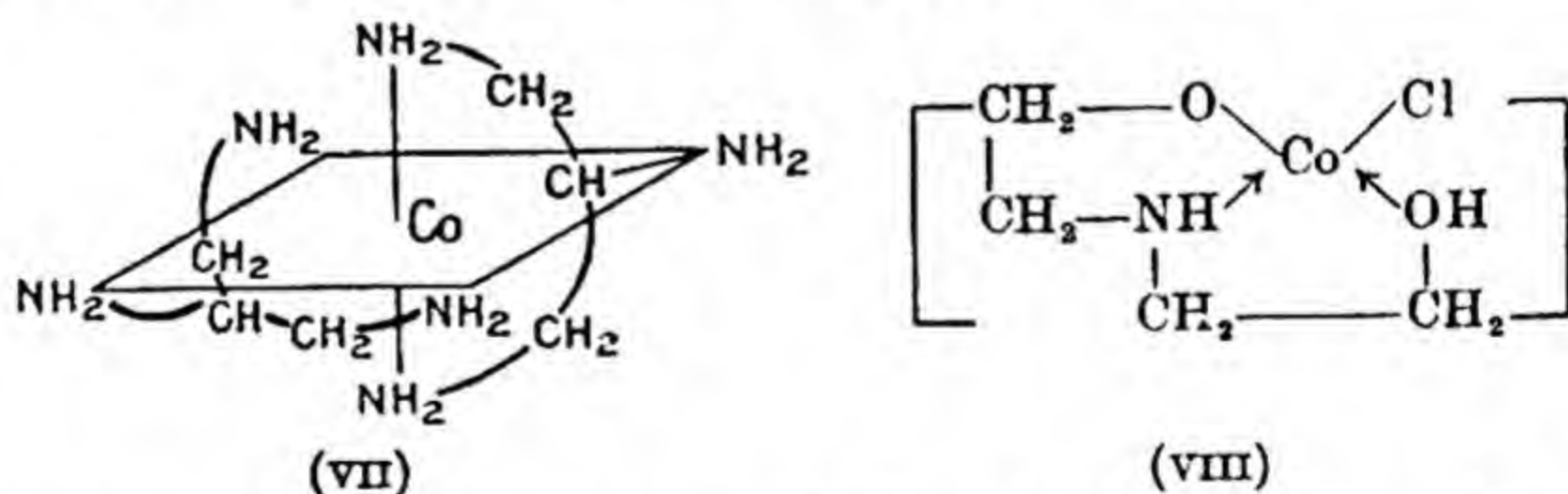
It is curious to note that, whereas the saturated 1,2-diamines (*e.g.* ethylenediamine, or 1,2-diaminocyclohexane) all act as chelating groups, *o*-phenylene diamine seems usually to be capable of filling only one co-ordination position.⁶⁷

Where chelate rings involving double bonds are formed, the formation of six-membered rings is favoured. It is thus the β -diketones which most readily give rise to inner complex salts from their enol forms. The formation of larger rings is not completely excluded: compounds have been described,^{68 69} (V) and (VI), containing the succinato and sulphonyldiacetic radicals, in which there are seven-membered and eight-membered rings respectively.



Tridentate and Quadridentate Groups.—In addition to the numerous bifunctional chelating groups, there are a few compounds known which are capable of filling three (*tridentate* groups) or even four (*quadridentate* groups) positions in the co-ordination shell.

As typical tridentate groups there may be cited tripyridyl, to which reference has already been made, and $\alpha\beta\gamma$ -triamino propane.⁷⁰ These form very stable compounds with the 6-co-ordinate metals, of the types $[\text{M tripy}_2]\text{X}_n$, $[\text{Co}\{\text{C}_3\text{H}_5(\text{NH}_2)_3\}_2]\text{X}_3$. In such compounds the co-ordinated group is probably attached in the 1,2,6 positions, along an octahedron edge (VII), and not in the vicinal



(1,2,3) positions bounding an octahedron face, as is shown by the fact that the same tridentate groups readily fill three co-ordination

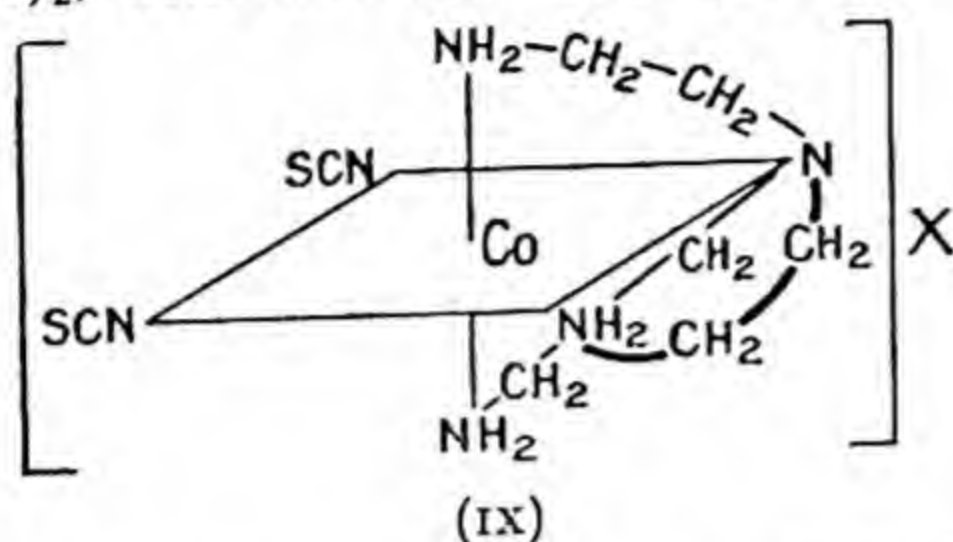
⁶⁷ Hieber, Schlieszmann and Ries, *Z. anorg. Chem.*, 1929, 180, 89; Hieber and Wagner, *Annalen*, 1925, 444, 249.

⁶⁸ J. C. Duff, *J.C.S.*, 1921, 119, 385.

⁶⁹ *Idem*, *ibid.*, 1921, 119, 1982; Slater-Price and Brazier, *ibid.*, 1915, 107, 1367.

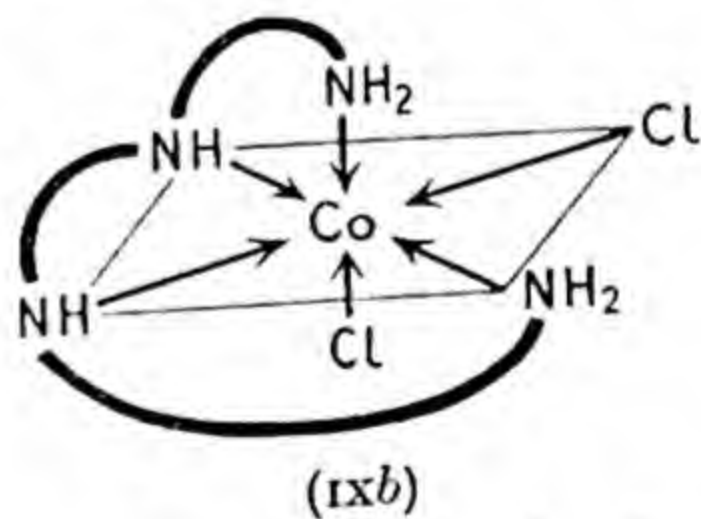
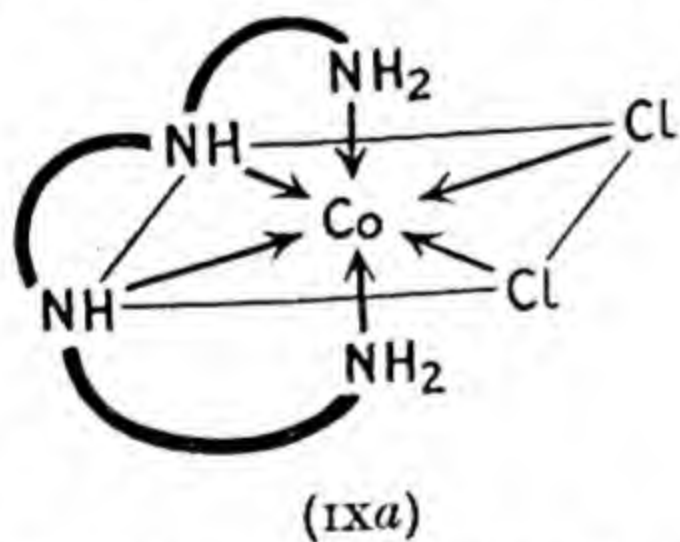
⁷⁰ W. J. Pope and F. G. Mann, *Proc. Roy. Soc.*, 1925, A, 109, 444; *J.C.S.*, 1926, 2675, 2681; 1927, 1224.

positions in the planar 4-co-ordinate complex, as in $[\text{Pt tripyCl}]\text{Cl}$. It may be shown, indeed, that such a structure is strainless only if the platinum atom and the whole tripyridyl molecule are coplanar. Inner complex salt formation by tridentate groups is also known; such compounds are formed, for example, by diethanolamine, $\text{NH}(\text{CH}_2\text{CH}_2\text{OH})_2$, with divalent cobalt (VIII).



Few quadridentate groups are known, since the possibility of such co-ordination requires the fulfilment of specialized geometrical conditions in order that a strain-free structure may result. The behaviour of $\beta\beta'\beta''$ -triaminotriethylamine as a tetrahedral quadridentate group has already been referred to (p. 143); it enters also into 6-co-ordinate structures, such as the cobaltic compound (IX).⁷¹

A further example of a tetrammine which is able to function as a quadridentate ligand, because of the flexibility of its molecular configuration, is afforded by 'triethylene tetrammine', $\text{NH}_2\cdot\text{C}_2\text{H}_4\cdot\text{NH}\cdot\text{C}_2\text{H}_4\cdot\text{NH}\cdot\text{C}_2\text{H}_4\cdot\text{NH}_2$. This forms a dichloro tetram-



mine cobaltic complex,⁷² and from analogies with the known isomers of the $[\text{Co Cl}_2 \text{en}_2]^+$ cation, this is believed to be the *cis* isomer (IXa) (or less probably (IXb)). The tetrammine is, however, able to wrap itself around four coplanar positions, since Jonassen and Cull⁷³ were able to prepare the Magnus salts $[\text{Pt trien}][\text{PtCl}_4]$ and $[\text{Pd trien}][\text{PdCl}_4]$.

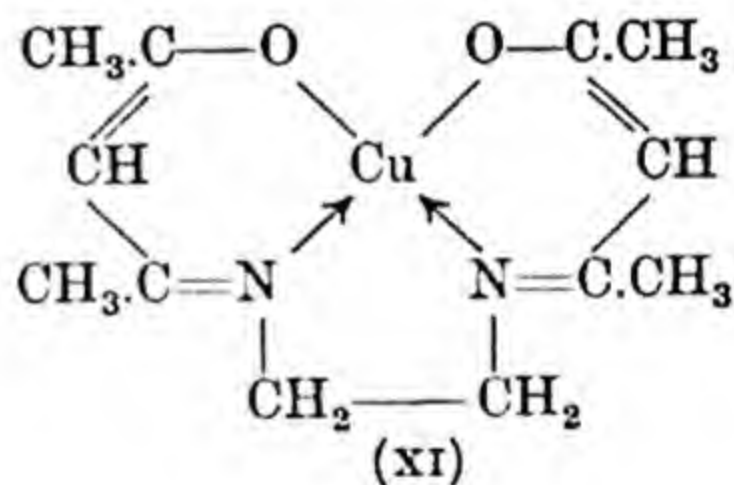
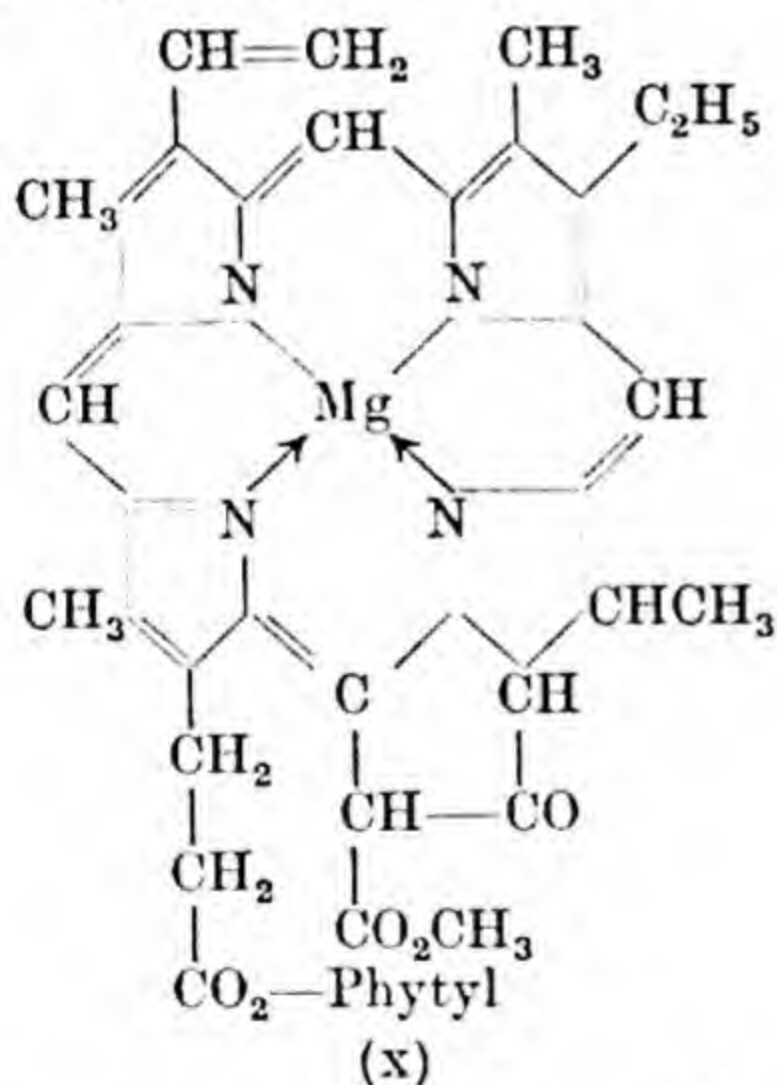
⁷¹ W. J. Pope and F. G. Mann, *J.S.C.I.*, 1925, 44, 834; Jaeger and Koets, *Z. anorg. Chem.*, 1928, 170, 347.

⁷² F. Basolo, *J. Amer. Chem. Soc.*, 1948, 70, 2631.

⁷³ *J. Amer. Chem. Soc.*, 1949, 71, 4097.

Of particular importance are quadridentate compounds in which the prosthetic groups are maintained in the spatial positions appropriate to a square planar configuration. This can be the case either because they are located in a larger cyclic structure, or because resonance in the organic skeleton of the ligand stabilizes a rigorously planar configuration of the whole.

To the first type belong the metal derivatives of the porphyrin skeleton, which are so deeply involved in the vital processes of both the vegetable and the animal kingdom. Chlorophyll (X), and the hæmin of blood, contain the magnesium and iron inner complex salts of porphyrin derivatives, and the oxidation-reduction properties of the iron porphyrin derivatives, and related compounds, appear to underlie the complex phenomena of biological oxidation. In porphyrin, as in the phthalocyanin structure referred to previously, the co-ordinating group forms a rigid planar structure of just such dimensions as to accommodate a metal ion. Structures of this type are attended with very great stability. Some of the metal phthalocyanines may be sublimed at a high temperature: in the case of the copper compound, the complex salt is stable in the vapour phase at 500° .

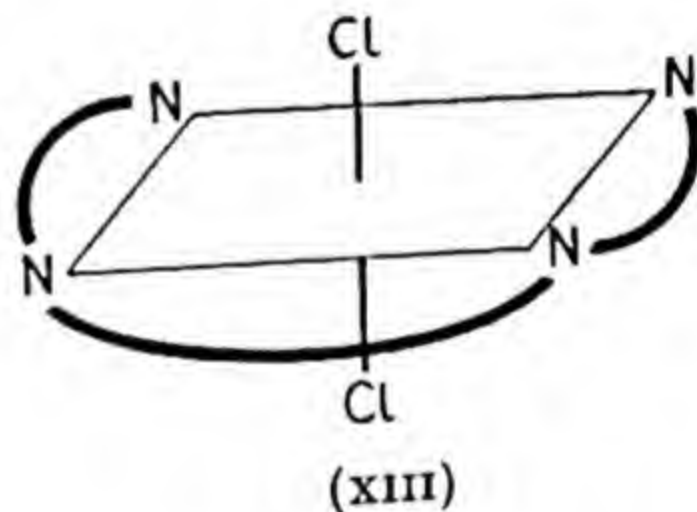
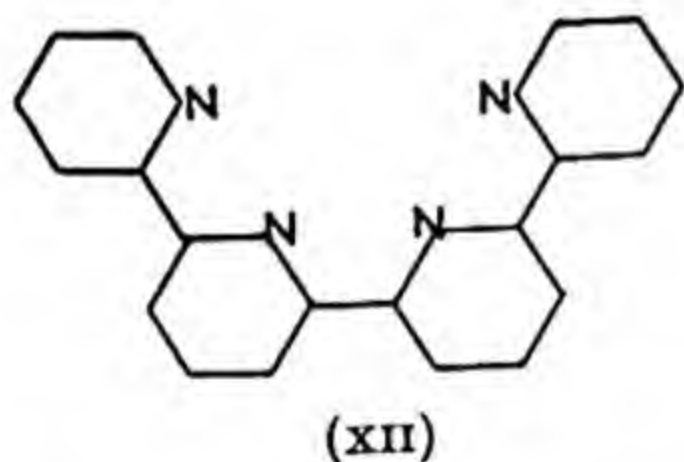


Similar great stability is shown by derivatives of quadridentate groups that fall rather into the second type. Thus the ethylene diimine derivatives of *o*-hydroxy-aldehydes (*e.g.* salicylaldehyde) and of β -diketones form some remarkably stable inner complex salts. The copper salt of bis-acetyl acetone ethylene diimine ⁷⁴ (XI), for

⁷⁴ G. T. Morgan and Main Smith, *J.C.S.*, 1925, 127, 2030.

example, may be heated almost to redness without suffering decomposition.

Reference is made elsewhere to the co-ordinating power of dipyridyl and tris-pyridyl, which function as neutral addenda, and not as inner-complex forming reagents. The great stability of the complex cations formed by them is undoubtedly connected with the planar configuration imposed by resonance. G. T. Morgan and F. H. Burstall⁷⁵ isolated, by pyrolysis of pyridine, some yet more highly condensed compounds, including the 'tetrapyridyl' (tetrapy) (XII), which can form co-ordination compounds with transition metals. Thus, with silver nitrate it forms $[\text{Ag tetrapy}]\text{NO}_3$; unlike $[\text{Ag dipy}_2]\text{NO}_3$, this is not oxidized by persulphate to a salt of bivalent silver. The bivalent metals Fe^{II} , Co^{II} , Ni , Cu , Zn all form compounds of the general formula $[\text{M tetrapy}]\text{X}_2 \cdot n\text{H}_2\text{O}$, and the pink cobalt (ii) complex is very readily oxidized to the grey-green the *trans* compound XIII, since the coplanar nature of the tetrapyridyl molecule requires that it be wrapped around four coplanar co-ordination positions.

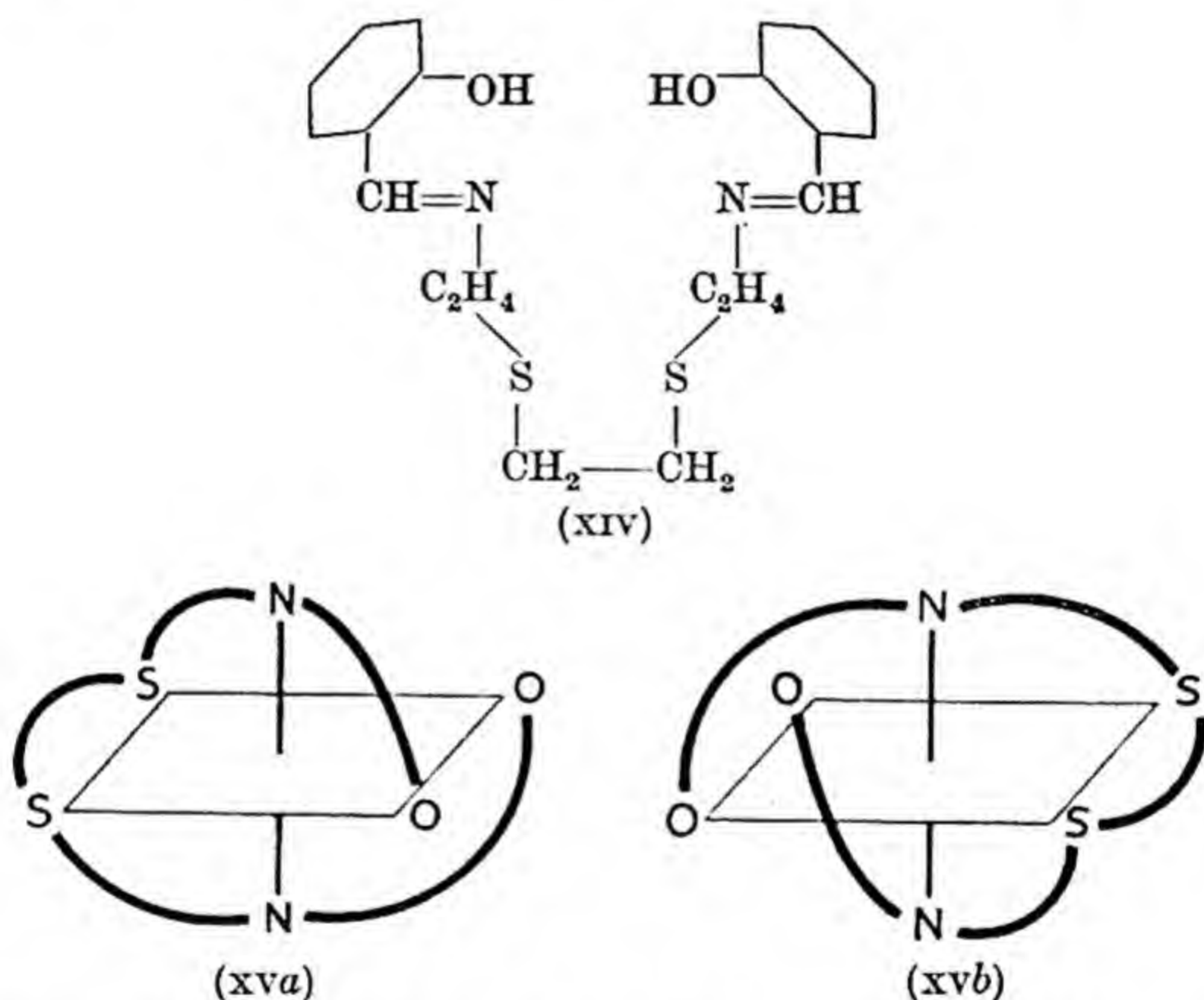


Sexadentate Groups.—Some remarkable polydentate groups have been described by Dwyer and Lions,⁷⁶ who have synthesized organic compounds containing six prosthetic groups (two acidic and four pure donors), all appropriately disposed in space for them to enter the co-ordination sphere of a single central atom. The salicylaldehyde derivative (XIV) (which may be denoted as SH_2) forms inner complex salts with the bivalent metals (Zn , Cu , Co and Ni)—of the formula $[\text{MS}]$. These are non-electrolytes, soluble in organic solvents such as chloroform. The orange-red cobalt complex, $[\text{CoS}]\cdot 3\text{H}_2\text{O}$, is oxidized by the air to a cobalt (iii) complex of intensely dark green colour, of which a series of salts $[\text{CoS}]\text{X}$ can be isolated. Dwyer and Lions found that this complex could be resolved by means of *d*-bromocamphor sulphonic acid into stable

⁷⁵ *J.C.S.*, 1938, 1672.

⁷⁶ *J.A.C.S.*, 1950, 72, 1545.

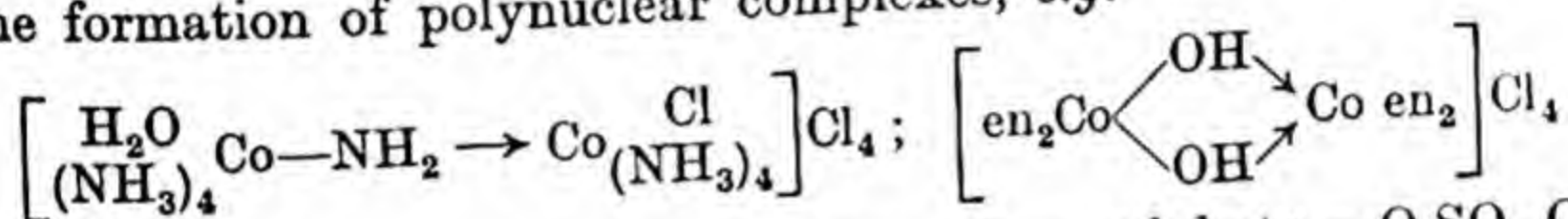
optical isomers, with extraordinarily high molecular rotation. Thus $[\text{CoS}]^+$ has $[\text{M}]_{5461}^{20} = \pm 50,160^\circ$, and the corresponding derivative of α -hydroxy β -naphthoic aldehyde has a molecular rotation of over $73,000^\circ$. It follows conclusively that the chelating radicle wraps itself around the central atom in the manner symbolized by (XVa) and (XVb), with the O and S atoms in *cis* positions, and the whole radicle constituting a right-handed or left-handed spiral. There are a few other known compounds which should be capable of filling six co-ordination positions in a similar interesting manner.



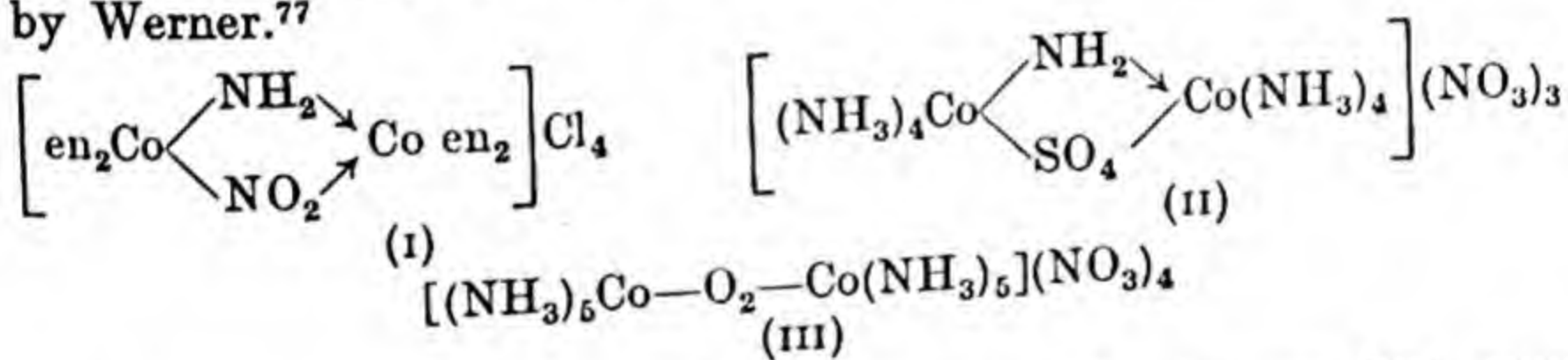
Polynuclear Complex Salts.—Reference was made, in discussing the stereochemistry of the cobaltammines, to the class of polynuclear complex salts. In these compounds, the co-ordination shells of two or more metallic atoms are joined by the sharing of one or more 'bridge' groups—such as the —OH groups in the salts already referred to. In the case of 6-co-ordinate complexes, it is plain that a corner, an edge, or a face may be held in common by two co-ordination octahedra, corresponding to the existence of one, two or three, but not more than three, bridges. Compounds of each class are known, and will be referred to in the following section.

Any neutral molecule or anion which is itself co-ordinatively unsaturated may act as a bridge group. It must be emphasized

that the distinction between the role of the central atom in co-ordination and that of the addenda is in a sense arbitrary, and a matter of convenience. The ammonia molecule occupies one place in the co-ordination shell because the co-ordination maximum, four, of the nitrogen atom is thereby attained; the old conception of the close relation between the amines and the ammonium salts, emphasized by Jörgensen, was in this sense correct. In the same way, the usual co-ordination number of oxygen is three, as in the oxonium salts $[R_3O]X$, so that a water molecule can form only one co-ordinate link, $H_2O \rightarrow M$. If, however, one hydrogen atom be removed, forming amido- or hydroxo-compounds, $M-NH_2$, or $M-OH$, the nitrogen and oxygen atoms become co-ordinatively unsaturated, and are then capable of forming additional co-ordinate links with other metallic atoms. They thereby act as bridges in the formation of polynuclear complexes, *e.g.*



The nitro $-NO_2$, peroxo $-O_2-$, oxo $-O-$, sulphato $-O.SO_2.O-$, acetato $-O.C(CH_3):O$, and other groups also enter into the formation of bridges, producing such compounds as (I), (II) and (III) below. The somewhat involved chemistry of these polynuclear cobalt and chromium amines was extensively worked out by Werner.⁷⁷

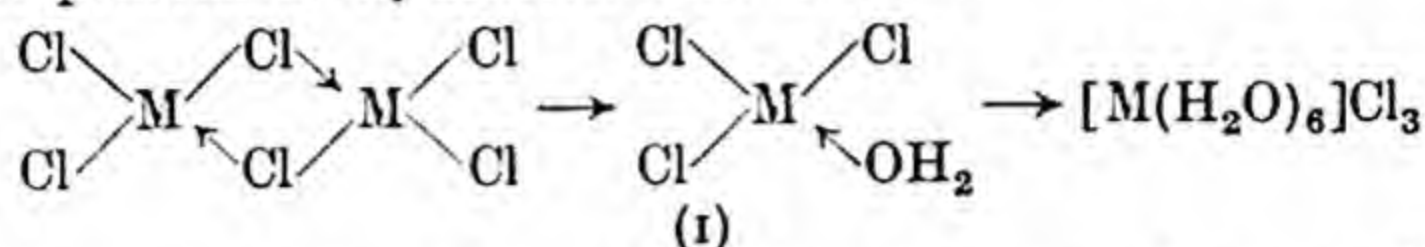


Polynuclear Halides.—In addition to the groups just considered, which serve as the linkage in polynuclear cobaltamines, the halogen atoms act as bridging groups in many compounds of the transition metals, and especially of the platinum metals. Indeed, the formation of polynuclear complexes by means of Cl (or Br) and OH bridges is a structural principle of some importance in several fields of inorganic chemistry.

Amongst the simple halides, this principle accounts for the existence of dimeric halides of gold, aluminium, iron, and probably of chromium and other metals, all conforming to the type M_2X_6 . The molecular complexity of aluminium and ferric halides, for example, has been established by vapour density measurements. The

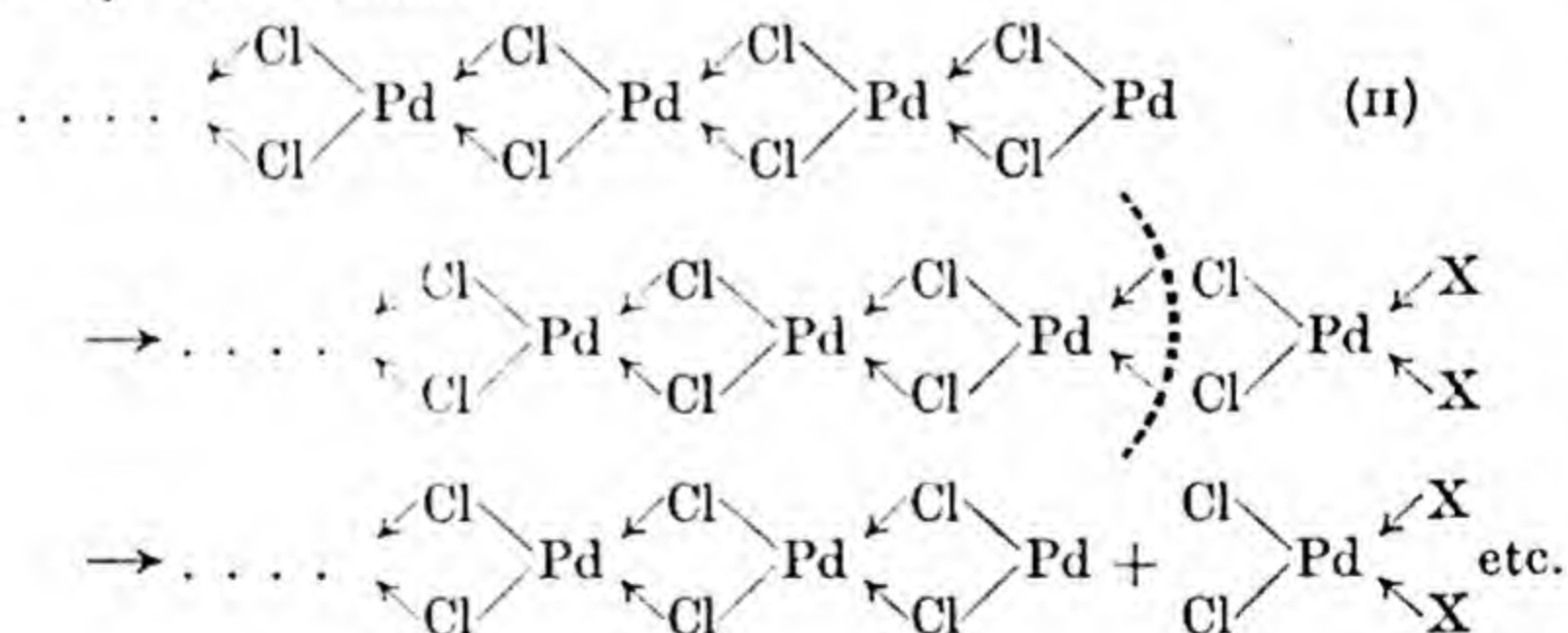
⁷⁷ *Annalen*, 1910, 375, 1.

molecular weight of gold bromide has been determined in benzene solution.⁷⁸ All these compounds are shown by their volatility, low electrical conductivity and their solubility in organic solvents to be non-electrolytes. From the crystal structure of aluminium bromide⁷⁹ and from electron diffraction measurements in the vapour of aluminium halides⁸⁰ it is evident that these compounds are correctly formulated as the bridged complexes (I), which can be converted into their electrolyte form only by an essentially chemical process of hydration and fission:



If an appropriate relationship exists between the co-ordination number of the metal and the formula of the stoichiometric unit, the process of halogen bridging may proceed further, to build up infinite polynuclear complexes, which enter as structural units into the crystals of the compounds concerned.

Thus, in palladous chloride $[\text{PdCl}_2]_\infty$, palladium atoms, each at the centre of a planar square of chlorine atoms, are linked through the chlorine bridges. The stereochemical requirements and the valency of palladium are thereby satisfied. Infinite strings (II) having the nett composition PdCl_2 therefore exist within the solid, and these react, or are dissolved by the action of polar molecules as shown by the schemes



where $\text{X} = \text{H}_2\text{O}$, Cl' , etc. In general, the fragments so stabilized are mononuclear or binuclear complexes only.

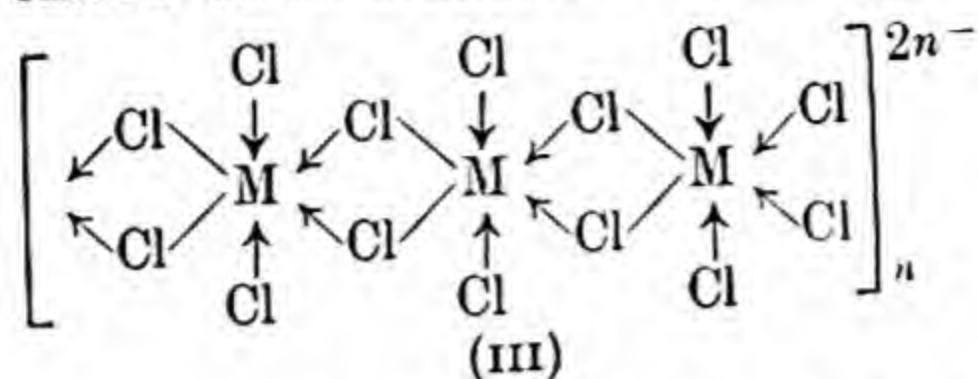
The same kind of 'inorganic high polymer' structures exist also as complex anions in a number of double halides. Thus the bivalent metals Zn, Cd, Hg and Sn usually have the co-ordination number 6,

⁷⁸ Burawoy and Gibson, *J.C.S.*, 1935, 217.

⁷⁹ Renes and MacGillivray, *Rec. Trav. Chim.*, 1945, 64, 276.

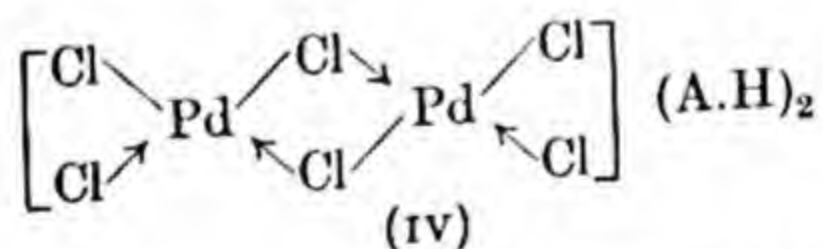
⁸⁰ Palmer and Elliot, *J.A.C.S.*, 1938, 60, 1309, 1852.

which is attained in the double salts $K_2[MCl_4]$ by halogen bridging (III), to form chains of co-ordination octohedra.



Comparable chains, but doubled and formed by a more complex mode of sharing halogen atoms, exist in the $[CdCl_3]^-$ and $[HgCl_3]^-$ anions. Complex anions of this kind exist, therefore, only within the solid crystalline salts. When they are dissolved in water, double halides of these types must either break up into their components, or else form solvated complex anions essentially different from those which build up the crystalline salts. This behaviour is to be contrasted with $K_2[PtCl_4]$, etc., in which the stereochemistry permits of the same discrete complex anion both in the solutions and as structural units in the crystallized salts.

The reactions of $PdCl_2$ and $PtCl_2$, especially, give rise to several types of complex halides which must be formulated as polynuclear structures. The first stage in degrading the infinite $[MCl_2]_\infty$ complex is probably to be seen in the double salts $A.HCl.PdCl_2$, formed by certain amines. These can be formulated as (IV). Further co-ordination of Cl^- ions produces the stable mononuclear anions $[PdCl_4]^{2-}$.



There is an extensive series of platinous compounds of the general formula $PtCl_2.X$, in which $X = PCl_3, P(OCH_3)_3, PR_3, AsR_3, CO, C_2H_4$, etc. ($R = \text{alkyl groups}$). It has been shown by Rosenheim and Löwen⁸¹ for $PtCl_2.P(OCH_3)_3$, by Anderson⁸² for $PtCl_2.C_2H_4$, and by Mann and Purdie⁸³ for the analogous palladium compounds of alkyl phosphines and arsines, that all these compounds are actually dimeric. Hence, apart from considerations of geometrical isomerism which will be discussed more fully below, they can be formulated on a common plan only if it is assumed that in all these compounds two chlorine atoms bridge the platinum or palladium atoms (V).

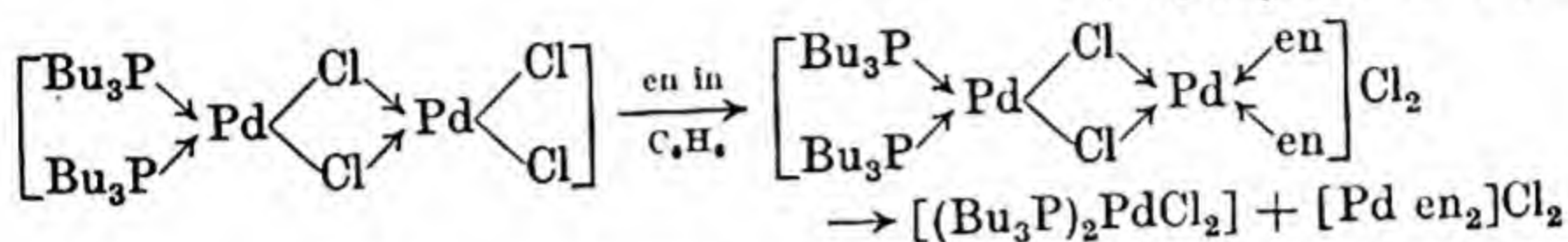
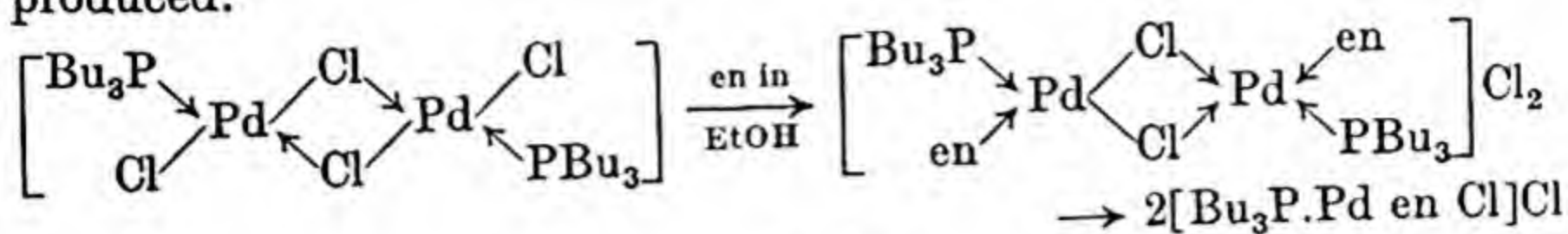
The structure of the platinum and palladium complexes referred to above must be planar, so that there should exist one unsym-

⁸¹ *Z. anorg. Chem.*, 1903, 37, 394; 1905, 43, 35.

⁸² *J.C.S.*, 1934, 971.

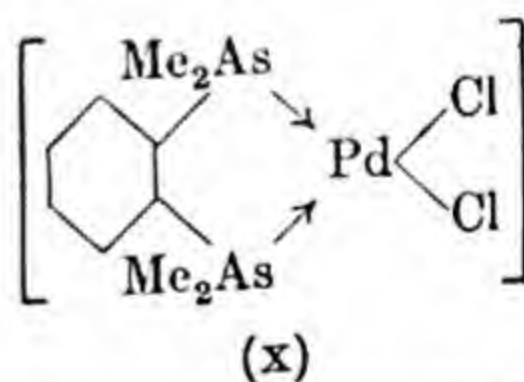
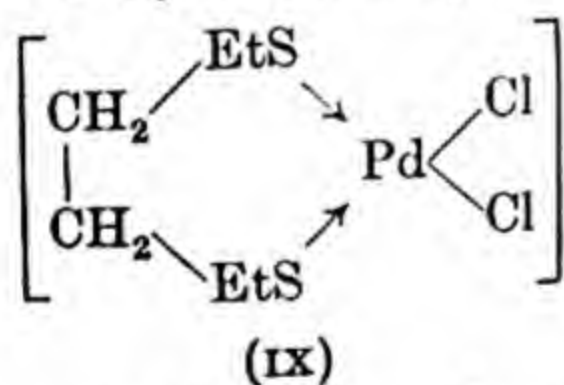
⁸³ *Ibid.*, 1936, 873.

in either form, according to the solvent used. In alcoholic solution, the compound behaves as if possessing the symmetrical formula, whereas in benzene derivatives of the unsymmetrical form are produced.



In view of this great mobility between the symmetrical and unsymmetrical forms, it is not surprising that any indication of geometrical isomerism between the two theoretically possible symmetrical forms (VII) and (VIII) is lacking.

At first sight, the balance of evidence may suggest that the phosphine and arsine compounds have, in fact, the unsymmetrical structure. However, in attempts to fix the unsymmetrical form, by using suitable chelating di-arsines or disulphides, Mann and Chatt⁸⁶ found that, in every case, the mononuclear compounds (IX) or (X) were without action on ammonium chloropalladite. If this implies that the unsymmetrical compounds are really unstable, the formation of their derivatives in reactions must indicate that some tautomeric equilibrium is set up in the solutions, such as could exist only in truly mobile systems



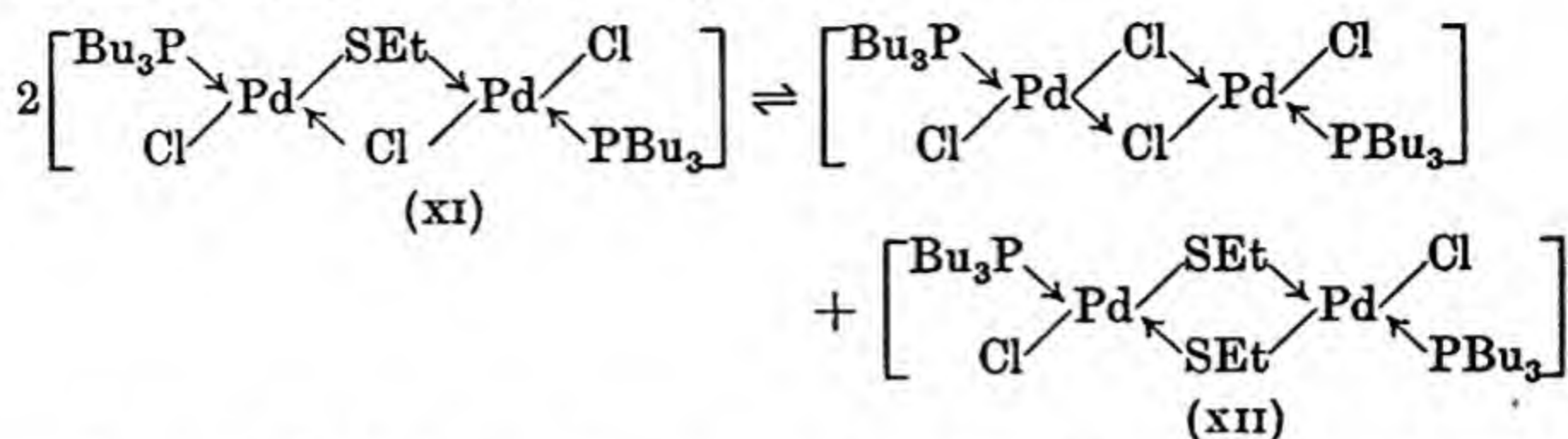
Mann and Chatt found evidence that this condition is fulfilled, since the mercapto-derivative (XI) gives, in solution, an equilibrium mixture of the simple phosphine and the di-thiol compound (XII).⁸⁷ The behaviour of these compounds may well be connected with the known instability of the geometrical isomers even of the simpler palladium complexes.

There is as yet no evidence of a similar mobility amongst the analogous compounds of platinum. It is possible that the various forms of these would exist as stable isomers, corresponding to the

⁸⁶ *Nature*, 1938 142, 709.

⁸⁷ *J.C.S.*, 1938, 1949.

much greater stability of *cis-trans* isomers amongst the platinous ammines than amongst the palladous ammines.

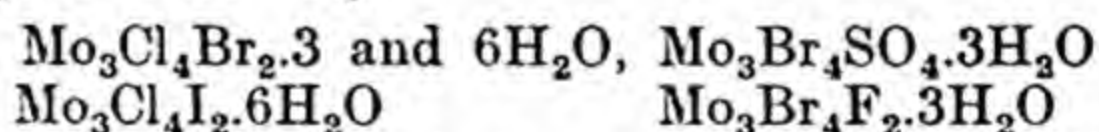


A particularly interesting group of polynuclear halides is formed by the lower halides of molybdenum and tantalum. Molybdenum trichloride and tribromide undergo disproportionation when they are heated in an inert atmosphere,⁸⁸ forming the so-called dihalides.

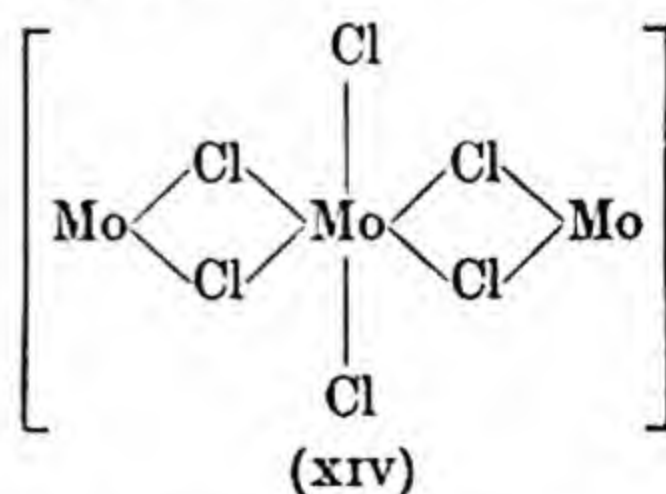
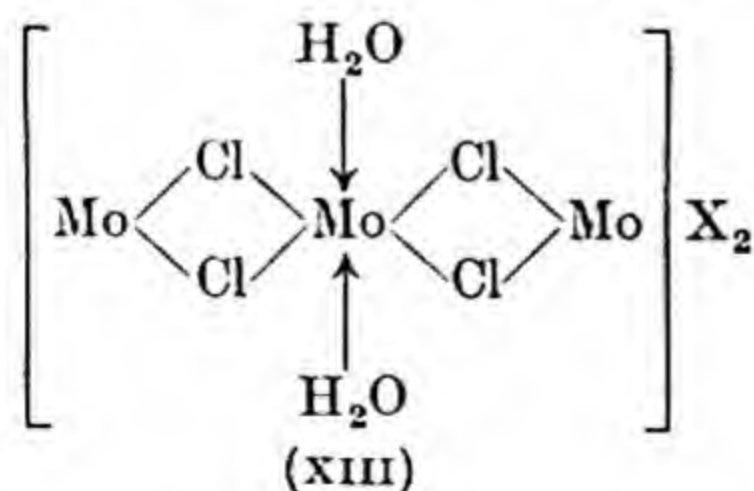


The dichloride so formed is insoluble in water, but is soluble in alkalis and in concentrated hydrochloric and hydrobromic acids. The chloride is also soluble in alcohol, and from its molecular weight in that solvent, determined ebullioscopically,⁸⁹ it was concluded that the compounds must possess the tripled formula, Mo_3Cl_6 and Mo_3Br_6 .

The trimeric formula accords also with the chemical evidence,⁹⁰ since the addition of acetic acid or of ammonium chloride to the solutions of the dihalides in caustic alkali precipitates well-defined hydroxides—*e.g.* $\text{Mo}_3\text{Br}_4(\text{OH})_2 \cdot 8\text{H}_2\text{O}$. These hydroxides are soluble in acids, and give salts—*e.g.*



It is clear that two of the six halogen atoms are mobile, and may be ionized, the rest being bound in a polynuclear cation. It is



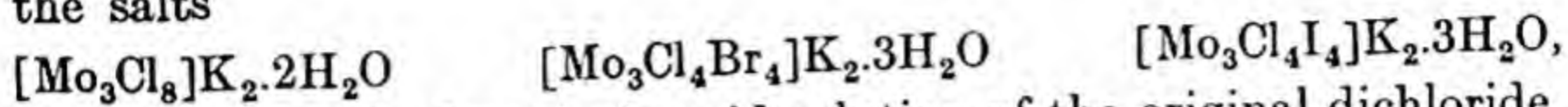
⁸⁸ Blomstrand, *J. prakt. Chem.*, 1857, **71**, 449; 1859, **77**, 88; 1861, **82**, 433; *Ber.*, 1873, **6**, 1464.

⁸⁹ *Ber.*, 1898, **31**, 2009.

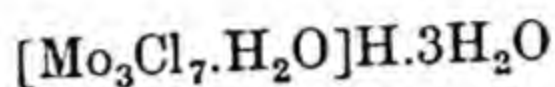
⁹⁰ Lindner, *Ber.*, 1922, **55**, 1458; *Z. anorg. Chem.*, 1923, **130**, 209; Rosenheim and Kohn, *ibid.*, 1910, **66**, 1.

significant also that all the salts are hydrated, and according to Lindner, two molecules of water are bound in the complex ion, which may perhaps be formulated as (XIII), derived from the original 'dichloride' (XIV).

The addition of halogen acids to the caustic alkaline solutions of the chloride yields compounds of a second type, namely, the alkali salts of trinuclear acids. There are obtained in this way the salts



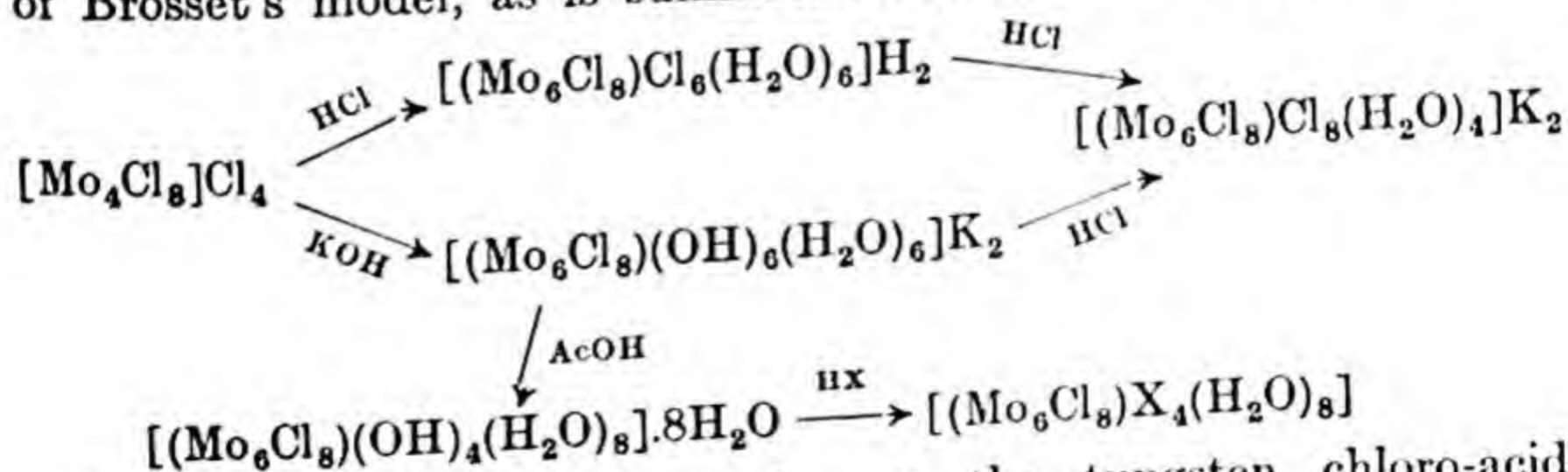
while from the hydrochloric acid solution of the original dichloride, the complex acid



and its pyridine, ethylenediamine, and aniline salts may be obtained.

The formulæ indicated were based by Lindner on purely chemical evidence. The essential soundness of the reasoning has since been verified by the independent physical evidence of X-ray crystallography. Brosset⁹¹ has found that, contrary to the ebullioscopic evidence, the structural unit should be doubled. All the compounds can then be derived from a cationic complex $[\text{Mo}_6\text{Cl}_8]^{4+}$, of unusual stereochemical configuration. Each chlorine atom of the complex is shared, as a bridge, between three molybdenum atoms. If the chlorine atoms are placed at the corners of a cube, the molybdenum atoms are then located just above the centre of each cube face, the whole building up a cubical cage. Although the metal atoms appear co-ordinatively unsaturated in this model, it may be noticed that in each of the known compounds the halogen atoms outside the polynuclear complex, together with water of hydration (or hydroxyl groups), would be sufficient to provide a total co-ordination number of 5 or 6 for each molybdenum atom.

On this basis, the older chemical results can be re-stated in terms of Brosset's model, as is summarized in the following table.

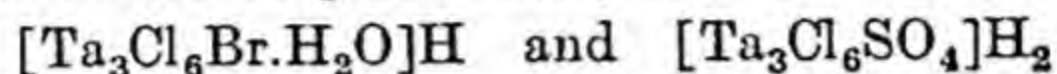


Related to these compounds are the tungsten chloro-acid $[\text{W}_3\text{Cl}_7]\text{H} \cdot 4\text{H}_2\text{O}$ prepared by Hill⁹² and the tantalum compounds

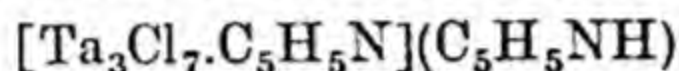
⁹¹ *Arkiv Kemi Min. Geol.*, 1946, 22A, No. 1.

⁹² *J. Amer. Chem. Soc.*, 1916, 38, 2383; cf. Lindner, ref. 90.

first obtained by Chapin⁹³ and reinvestigated by Lindner.⁹⁴ The latter compounds were obtained by reducing tantalum pentachloride with metallic lead at 600°. By extracting the melt with hydrochloric acid, a dark green crystalline compound, $\text{Ta}_3\text{Cl}_6 \cdot \text{HCl} \cdot 4\text{H}_2\text{O}$, is obtained, which loses only $3\text{H}_2\text{O}$ below 200°. One molecule of water is thus constitutional, and the substance is presumably an acid with the anion $[\text{Ta}_3\text{Cl}_7 \cdot \text{H}_2\text{O}]'$, corresponding to that of the molybdenum chloro-acid. In this anion, one chlorine has unique properties, since if hydrobromic acid or sulphuric acid be used for the extraction of the original melt, the analogous compounds



are formed. By the action of pyridine, salts are formed, with the simultaneous replacement of the water inside the complex, giving



While this interpretation of the reactions has been contested by Ruff and Thomas,⁹⁵ it is probably to be accepted as being in best accord with the co-ordination theory, and with the analogous compounds of molybdenum. It is very suggestive that the derivatives of all three metals can be interpreted in terms of a common type of polynuclear structural unit, $[\text{A}_3\text{Cl}_8]^{4+}$.

Prussian Blue.—A striking illustration of the manner in which the requirement of attaining the stable co-ordination number may bring about the polymerization of inorganic compounds is afforded by prussian blue and the compounds related to it. The key to the constitution of these compounds, which has for many years been in dispute, has been supplied by the X-ray analysis of their structure.

Substances termed α , β , and γ soluble prussian blue have been described in the literature. In reality all these compounds are insoluble, differing only in the ease with which they may be dispersed colloiddally, and they are actually identical, with the general formula $\text{RFe}[\text{Fe}(\text{CN})_6]$ (where R = an alkali metal, usually K). Since soluble prussian blue can be formed either by the action of ferrous salts on ferricyanides, or of ferric salts on ferrocyanides, the formula might be written either as $\text{KFe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]$ or as $\text{KFe}^{\text{II}}[\text{Fe}^{\text{III}}(\text{CN})_6]$. The chemical evidence is conflicting.⁹⁶ Thus, sodium hydroxide converts prussian blue to ferric hydroxide

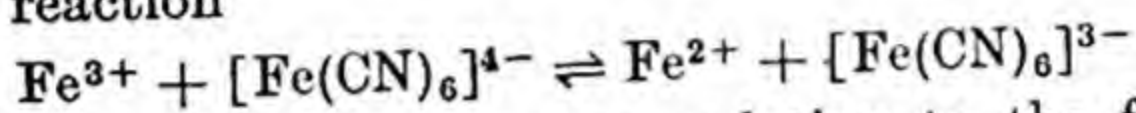
⁹³ *J. Amer. Chem. Soc.*, 1910, 32, 324.

⁹⁴ *Ber.*, 1922, 55, 1458; *Z. anorg. Chem.*, 1924, 137, 66.

⁹⁵ *Ber.*, 1922, 55, 1466; *Z. anorg. Chem.*, 1925, 148, 1, 19.

⁹⁶ Cf. K. A. Hofmann *et al.*, *Annalen*, 1904, 337, 1; 1907, 352, 54; Eibner and Gerstacker, *Chem. Ztg.*, 1913, 37, 137, 178, 195; Muller, *ibid.*, 1914, 38, 281, 328; Woring, *J. prakt. Chem.*, 1914, [ii], 89, 51.

and sodium ferrocyanide, whereas ammonium carbonate forms ammonium ferricyanide. Equally ambiguous is the formation of prussian blue from ferric ferricyanide, $\text{Fe}^{\text{III}}[\text{Fe}^{\text{III}}(\text{CN})_6]$, by reduction either with hydrogen peroxide (which reduces ferricyanides, but not ferric iron) or with sulphur dioxide (which reduces ferric iron but not ferricyanides). The chemical identification of prussian blue as a ferric ferrocyanide derivative seems to be confirmed, however, by the fact that the formation of soluble prussian blue is a slow reaction, which is accelerated by the ions Fe^{2+} , $[\text{Fe}(\text{CN})_6]^{3-}$ and $[\text{Fe}(\text{CN})_6]^{4-}$, but retarded by ferric ions. This last effect can only be in virtue of their role in removing ferrocyanide by the equilibrium reaction



An examination of the literature relating to the ferrocyanides suggests that in addition to soluble prussian blue and the white insoluble ferrous ferrocyanides $\text{R}_2\text{Fe}[\text{Fe}(\text{CN})_6]$, other heavy metal compounds must be differentiated, in virtue of their colour and insolubility, from the true salts. The simple ferrocyanides—*e.g.* the alkali salts and $\text{Ca}_2\text{Fe}(\text{CN})_6$ —are yellow, rather soluble compounds, as also are the ferrocyanides of complex amines, which possess mixed colours. The heavy metal ferrocyanides may be typified by the brown insoluble copper salt, usually formulated as $\text{Cu}_2\text{Fe}(\text{CN})_6 \cdot 7$ or $10\text{H}_2\text{O}$ (Hatchett's brown). That this is not a simple salt is proved by its reactions, as well as by its colour. Thus, on boiling with solutions of the alkaline earth ferrocyanides, the well-crystallized salts $\text{R}[\text{CuFe}(\text{CN})_6]$ (where $\text{R} = \text{Ca}, \text{Sr}, \text{Ba}$) are obtained, while with dilute aqueous ammonia the ammine $\text{Cu}_2\text{Fe}(\text{CN})_6 \cdot 4\text{NH}_3 \cdot \text{H}_2\text{O}$ or $[\text{Cu}(\text{NH}_3)_4][\text{CuFe}(\text{CN})_6] \cdot \text{H}_2\text{O}$ is formed. The original copper ferrocyanide should therefore be formulated as $[\text{Cu}(\text{H}_2\text{O})_4][\text{CuFe}(\text{CN})_6] \cdot 3$ or $6\text{H}_2\text{O}$ —*i.e.* as the salt of a polynuclear complex anion $[\text{CuFe}(\text{CN})_6]^{2-}$, comparable with the complex of ferrous ferrocyanide, or of prussian blue.

The nature of the complex anion in the prussian blues is revealed by Keggin's X-ray analysis.⁹⁷ All the compounds may be regarded as derived from the structure of ferric ferricyanide or Berlin green, $\text{Fe}[\text{Fe}(\text{CN})_6]$. This has a cubic crystal lattice, the unit cell being of 5.1 \AA side. A cubical block of eight unit cells is represented in Fig. 29, *A*, for comparison with the structures of soluble prussian blue and ferrous ferrocyanide. In the former compound (Fig. 29, *B*), which is also cubic, with $a = 10.2 \text{ \AA}$, the essential skeleton is preserved but alternate iron atoms are reduced to the ferrous state; the cell dimensions are thereby doubled. An alkali metal

⁹⁷ *Nature*, 1936, 137, 577.

ion is inserted in every alternate small cube giving the formula $\text{KFeFe}(\text{CN})_6$. In ferrous ferrocyanide, all the iron atoms are reduced to the ferrous state. The cell dimension is again 5.1 Å, and every small cube is occupied by an alkali ion as is required by the formula $\text{K}_2\text{FeFe}(\text{CN})_6$ (Fig. 29, C). The iron atoms of prussian blue cannot be distinguished as ferrous and ferric ions; it is far more likely that they are equivalent, and that the valency state and charge distribution are evened out by a resonance process in the way discussed elsewhere in this chapter. With this view the bronzy lustre and deep colour of the pigment are in full accord. Precisely the same structure, apart from minor differences in lattice dimensions, is found in the cupriferricyanides $\text{MCuFe}(\text{CN})_6$ and in ruthenium purple,⁹⁸ $\text{MFeRu}(\text{CN})_6$; in each case (ferrous) iron is substituted atom for atom by the second metal.

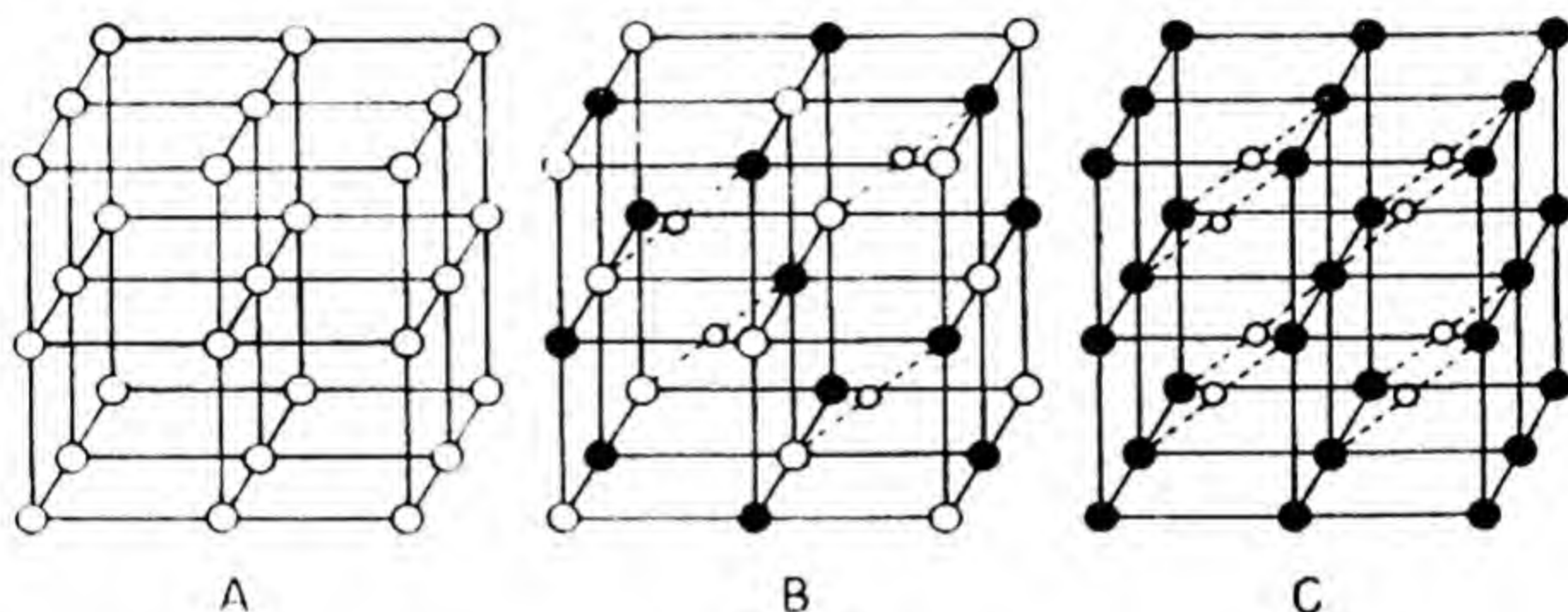
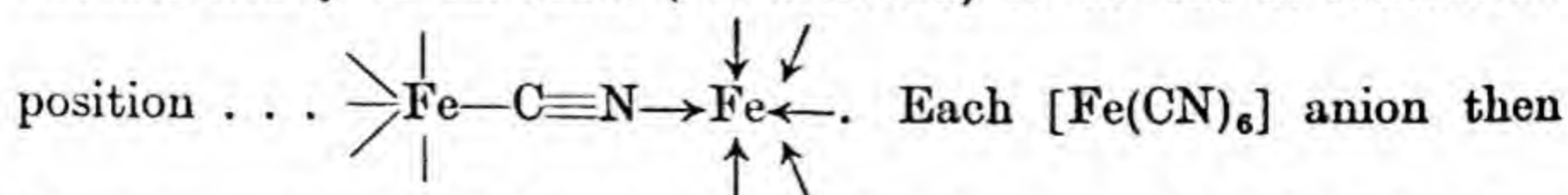


FIG. 29.

The position of the cyanide groups was not determined by the X-ray analysis, but the following considerations fix them with certainty, and lead to the important conception of *supercomplex formation*. This arises from the fact that the $(\text{CN})^-$ group as a co-ordinating unit is double-ended, as has already been seen, and could co-ordinate by means of either its carbon or its nitrogen atom. In the ferrocyanides, the evidence of alkylation suggests that the carbon atoms are attached to the central atom of iron. The nitrogen of each cyanide group can then co-ordinate with another heavy metal atom (*i.e.* a cation) to fill one co-ordination



becomes surrounded by six attached cations, and each cation by

⁹⁸ J. L. Howe, *J. Amer. Chem. Soc.*, 1898, 18, 981.

six $[\text{Fe}(\text{CN})_6]$ groups. The whole builds up an infinite three-dimensional network identical with that found by Keggin. The union of ferricyanide ions with ferric cations then gives Berlin green; that of ferrocyanide with ferric or ferrous ions gives supercomplex anions which we may denote non-committally by the structural units $[\text{Fe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]]^-$ and $[\text{Fe}^{\text{II}}[\text{Fe}^{\text{II}}(\text{CN})_6]]^{2-}$, respectively. The former, as Davidson has suggested,⁹⁹ may conveniently be termed berlinic acid, and the soluble prussian blues are then berlinates. The action of excess ferric iron on a ferrocyanide may then be represented as forming a ferric berllinate $\text{Fe}[\text{Fe}[\text{Fe}(\text{CN})_6]]_3$, rather than a true ferric ferrocyanide $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ as is usually written, while an excess of ferrous iron with a ferricyanide similarly gives $\text{Fe}[\text{Fe}[\text{Fe}(\text{CN})_6]]_2$ rather than true ferrous ferricyanide. In this way, the formation of alkali-free prussian blues is explicable.

In the heavy metal ferrocyanides we have exactly comparable heterometallic supercomplexes; the copper compound, for example, being $\text{R}_2[\text{Cu}[\text{Fe}(\text{CN})_6]]$. Where, however, the second metal atom has a co-ordination number less than six, the supercomplex must conform to a less simple type. Thus, zinc ferrocyanide, nominally $\text{Zn}_2[\text{Fe}(\text{CN})_6]$, reacts with potassium ferrocyanide to form $\text{K}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$. Zinc, with a valency of two, has a co-ordination number of four. Hence, on the average, two ferrocyanide residues can form a supercomplex with three atoms of zinc— $[\text{Zn}_3[\text{Fe}(\text{CN})_6]_2]^{2-}$, making the formula of normal zinc ferrocyanide, $\text{Zn}[\text{Zn}_3[\text{Fe}(\text{CN})_6]_2]$. The cuproferrocyanides are similarly constituted. Silver ferrocyanide gives rise in the same way to $\text{KAg}_3[\text{Fe}(\text{CN})_6]$. Here, since silver has a co-ordination number (usually) of two, the supercomplex has the formula $[\text{Ag}_3[\text{Fe}(\text{CN})_6]]^-$, and the normal silver salt, $\text{Ag}_4[\text{Fe}(\text{CN})_6]$, is probably $\text{Ag}[\text{Ag}_3[\text{Fe}(\text{CN})_6]]$.

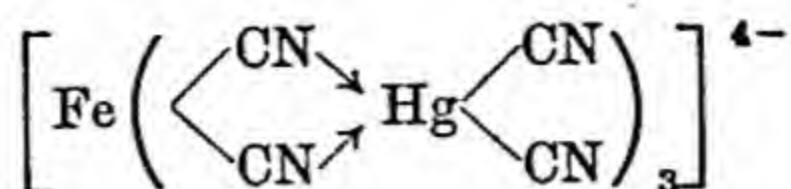
The existence of such supercomplexes provides a clue to the understanding of a number of anomalies in the complex cyanides of metals other than iron. This was pointed out much earlier by Reihlen and Zimmermann,¹⁰⁰ although these authors attempted to formulate the structures concerned upon a faulty basis. Thus, the action of a deficiency of alkali cyanide upon manganous salts gives a green insoluble compound of the empirical formula $\text{KMn}(\text{CN})_3$. This can now be interpreted as $\text{K}_2[\text{Mn}[\text{Mn}(\text{CN})_6]]$ by analogy with ferrous potassium ferrocyanide; its extreme insolubility is at once comprehensible. The so-called $\text{NaZn}(\text{CN})_3 \cdot 5\text{H}_2\text{O}$ can probably be formulated similarly. In Strömholm's salts,¹⁰¹ $\text{R}_4\text{Fe}(\text{CN})_6 \cdot 3\text{Hg}(\text{CN})_2$,

⁹⁹ *J. Chem. Education*, 1937, 14, 238, 277.

¹⁰⁰ *Annalen*, 1927, 451, 75.

¹⁰¹ *Z. anorg. Chem.*, 1914, 84, 208.

it is possible that—as Strömholm suggested—there is a polynuclear anion



which constitutes an intermediate stage between a simple complex cyanide and the supercomplex structures discussed above.

Polynuclear Compounds and Anomalous Valency.—In the cases considered, the metallic atoms serving as co-ordination centres have been in the same valency state. If, however, two atoms of differing valency may form a polynuclear complex, the principles applied in the preceding sections may be extended to explain certain cases of anomalous valency.

Thus, a number of compounds of seemingly trivalent platinum and palladium are known, in which the metal apparently has the co-ordination number 5. To this group of compounds belong Jörgensen's $(\text{NH}_3)(\text{C}_2\text{H}_5\text{NH}_2)\text{PtBr}_3$,¹⁰² and the similar substances $(\text{NH}_3)(\text{C}_5\text{H}_5\text{N})\text{PtCl}_3$ and $(\text{NH}_3)_2\text{PdCl}_3$,¹⁰³ which are formed by the mild oxidation of the corresponding diammine platinous salts. These compounds are undoubtedly non-electrolyte complexes, and they possess strikingly deep colours—*e.g.* the palladium compound cited is black. Drew, Pinkard, Wardlaw and Cox¹⁰³ tentatively formulated these compounds with metal to metal bonds, as in (I). It appears to be a general principle, however, that covalent links are never formed between metal atoms. This type of formulation may be avoided, as was pointed out by Mann,¹⁰⁴ if the compounds are regarded as constituted as (II), (III), in which one quadrivalent and one bivalent metal atom are linked by the Cl bridge. The states of the two atoms differ only in that the one possesses two electrons more than the other; in such a case, a state of 'resonance' may be set up, in which the electron density distribution is statistically evened out. Where this kind of possibility arises from the presence of atoms of the same element in different valency states—*e.g.* in Pb_3O_4 , Mo_3O_8 , prussian blue, etc.—an intense colour frequently results. The trivalency of the platinum and palladium is thus only formal. Some support for the view here outlined is provided in that the related compounds $[\text{en PtCl}_3]$ and $[(\text{NH}_3)(\text{EtNH}_2)\text{PtCl}_3]$ may be formed¹⁰⁵ not only by the oxidation of the corresponding platinous compounds, but also by the direct combination of $[\text{en PtCl}_2]$ with $[\text{en PtCl}_4]$, and of

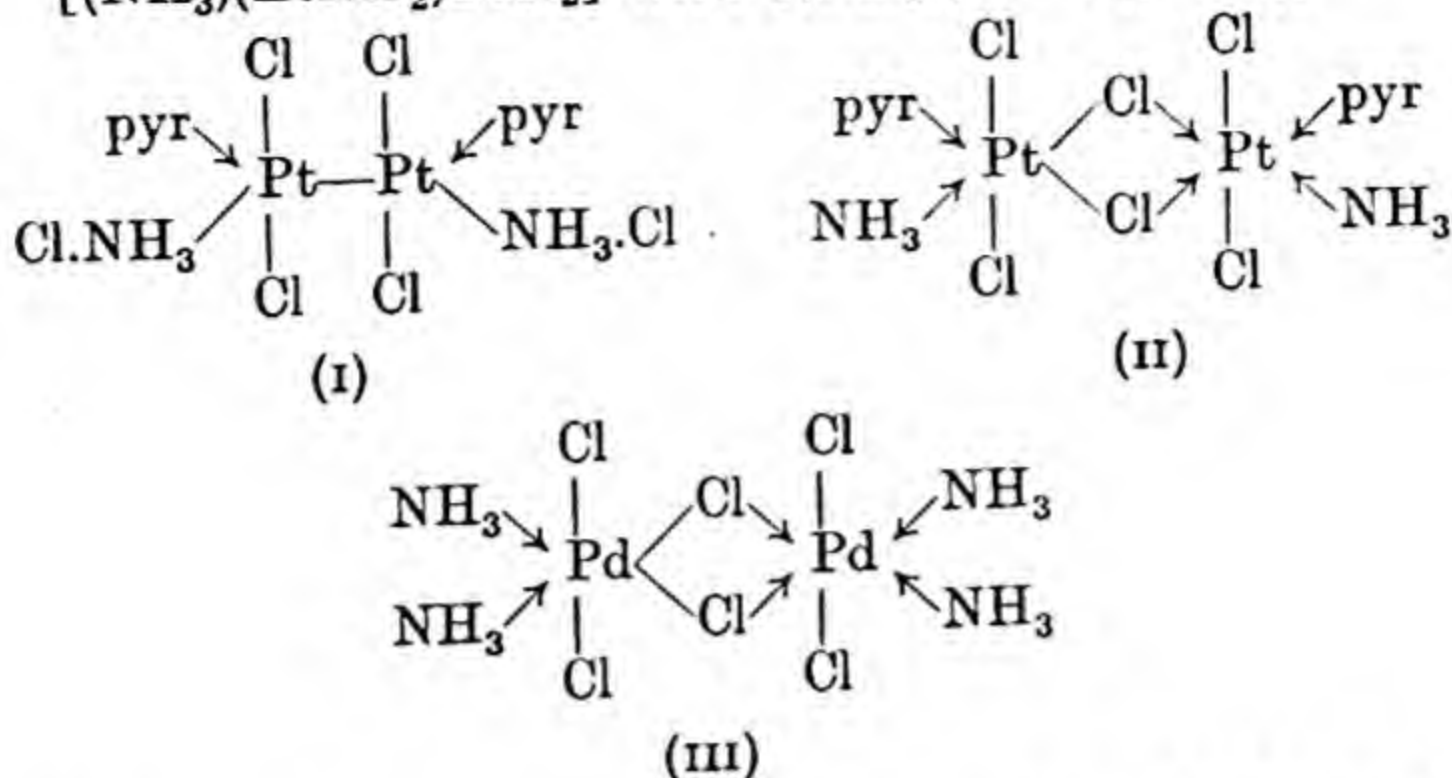
¹⁰² *J. prakt. Chem.*, 1886, 33, 489.

¹⁰³ *J.C.S.*, 1932, 1013, 1898.

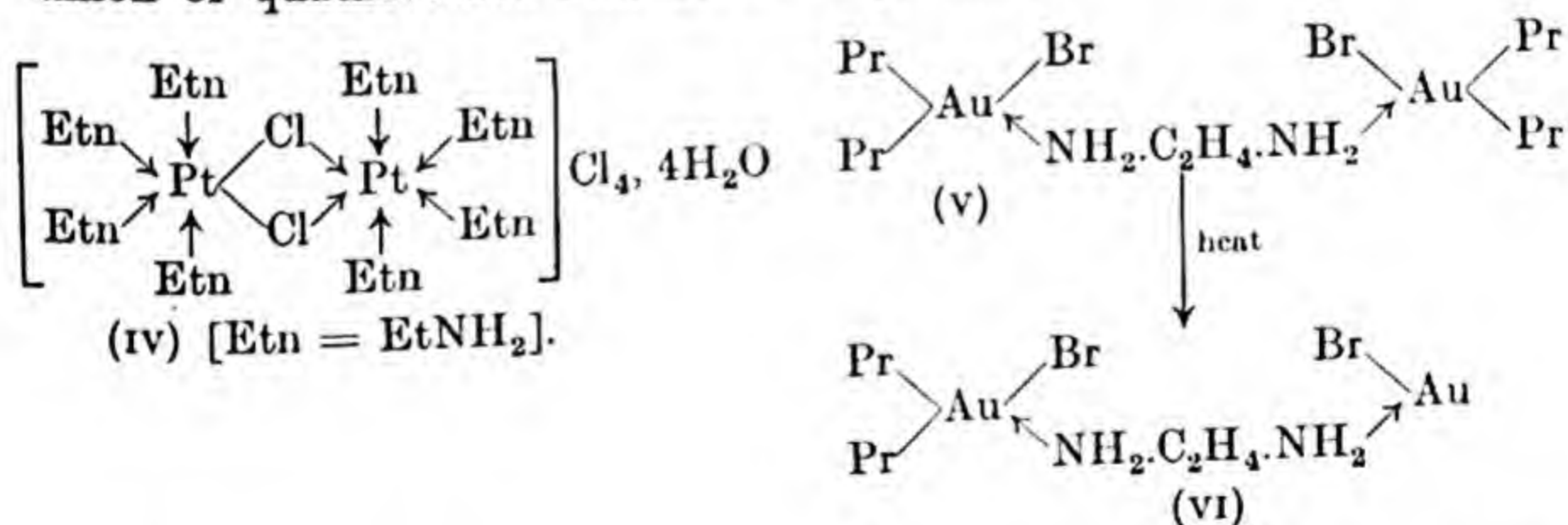
¹⁰⁴ *Ibid.*, 1936, 873.

¹⁰⁵ Drew *et al.*, *ibid.*, 1935, 1246.

$[(\text{NH}_3)(\text{EtNH}_2)\text{PtCl}_2]$ with $[(\text{NH}_3)(\text{EtNH}_2)\text{PtCl}_4]$.



A further case in which such a structure is probable is that of Wolfram's red salt, $(\text{EtNH}_2)_4\text{PtCl}_3 \cdot 2\text{H}_2\text{O}$, which is obtained by the mild oxidation of $[\text{Pt}(\text{EtNH}_2)_4]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$. Reihlen and Flohr¹⁰⁶ found that the same compound crystallized from solutions containing $[\text{Pt}(\text{EtNH}_2)_4]\text{Cl}_2$ and $[\text{Pt}(\text{EtNH}_2)_4\text{Cl}_2]\text{Cl}_2$, in equimolecular proportions, while Wolfram's salt in solution gave the characteristic reactions of both these substances. They concluded that it was merely a lattice compound of the platinous and platinic components. Drew and Tress^{106a} showed that the salt is, indeed, largely or entirely dissociated in solution, only two-thirds of the chlorine being ionized. It is probable that it exists only in the crystalline solid state, and it may be represented (IV) as of the same type as the other compounds of 'trivalent' platinum, being formed by the co-ordinative union of quadrivalent and bivalent platinum.



A compound of gold which undoubtedly contains both univalent and trivalent gold, joined co-ordinatively, has been described by Gibson.¹⁰⁷ The auric *n*-propyl compound (V) loses two propyl radicals (in the form of hexane) when its solutions in benzene or

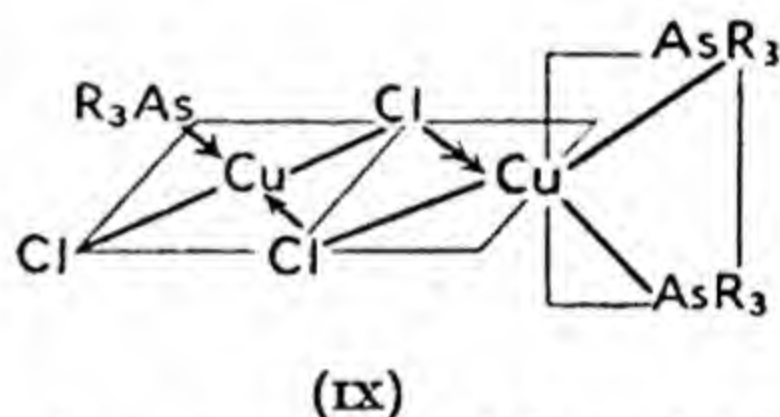
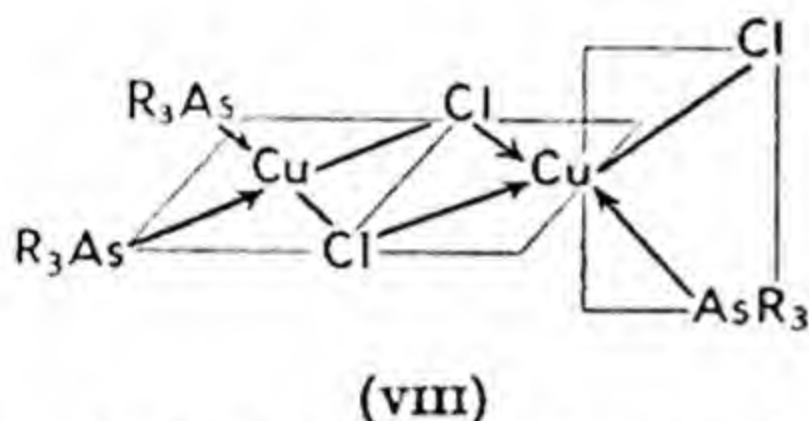
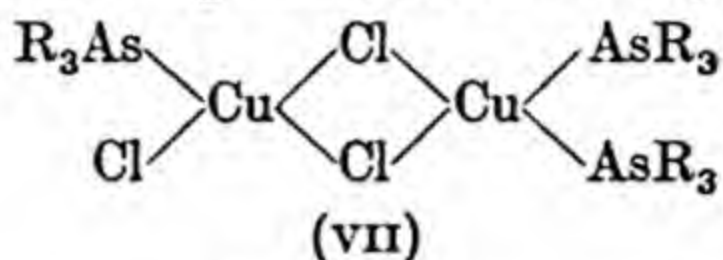
¹⁰⁶ *Ber.*, 1934, 67, 2010.

^{106a} *J.C.S.*, 1935, 1244.

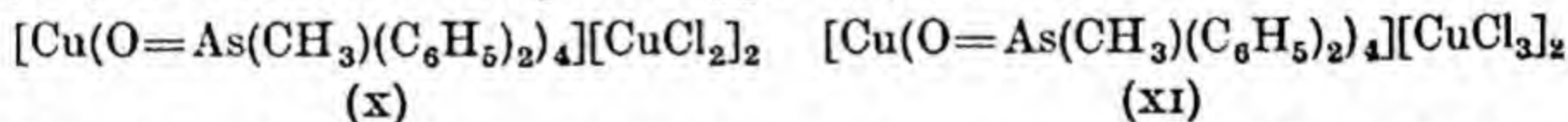
¹⁰⁷ *Ibid.*, 1935, 219.

chloroform are heated, and the product of the reaction cannot well be formulated other than as (VI). In this compound, the aurous atom has the co-ordination number two, as in $\text{K}[\text{Au}(\text{CN})_2]$.

In certain circumstances the presence, within the same molecule, of two co-ordination centres, differing in their valency and their stereochemical configuration, might give rise to novel types of isomerism. Mellor, Burrows and Morris¹⁰⁸ believed this to be the explanation of a pair of compounds obtained by the action of diphenyl methyl arsine on cupric chloride. On the basis of chemical analyses, both the blue and brown forms were assigned the same formula (VII), representing a compound containing both Cu^{I} and Cu^{II} . Since Cu^{II} has the square planar configuration, and Cu^{I} the



tetrahedral configuration, such a binuclear complex might exist in the isomeric forms (VIII) and (IX). However, a fuller investigation of the chemistry of these substances^{108a} has proved that the two forms are neither isomers nor polynuclear complexes, but that they probably represent the cuprochloride (X) and the cuprichloride (XI) of the same complex copper (ii) cation.



The analytical differences between formulæ (VII), (X) and (XI) (which could not be isolated in the pure state) are relatively small. It is evident from such cases as this, and the supposed isomerism of dimethyl tellurium iodide (p. 126), that in every case the relevant chemical evidence must be critically sifted before weight can be attached to supposed instances of stereoisomerism.

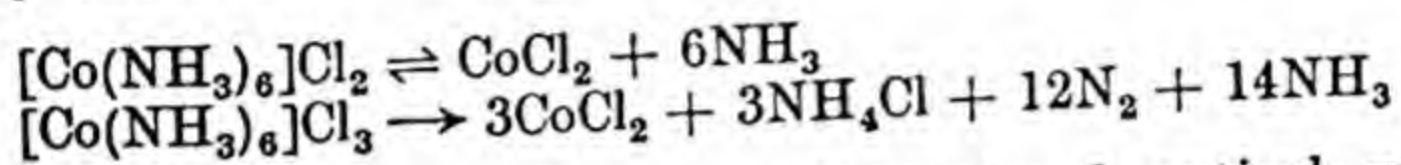
THE NATURE OF THE CO-ORDINATE LINKAGE

In the foregoing sections, the term co-ordination has been used as far as possible without reference to any special valency concep-

¹⁰⁸ *Nature*, 1938, 141, 414.

^{108a} R. S. Nyholm, *J.C.S.*, 1951, 1767.

tions, and without distinguishing between the operation of true chemical valencies and of undirected electrostatic attractions. Reference has been made to the division of salt ammoniates by Biltz into two classes, which may be typified by hexamine cobaltic chloride and cobaltous chloride ammoniate, respectively. The most immediately obvious difference between these two classes is that, whereas the ammoniates and allied compounds (termed by Biltz *normal* complexes) dissociate reversibly into their components, hexamine cobaltic chloride and similar complexes do not display any reversible dissociation pressure of ammonia below that temperature at which complete irreversible dissociation takes place, whereby ammonia is oxidized in part to nitrogen.



Several lines of evidence, based on dimensional, optical, magnetic and stereochemical considerations, combine to show that in the 'penetration' complexes, the co-ordinated complex is bound together by true directed chemical valencies, and it is perhaps permissible to identify the two classes postulated by Biltz with the operation of chemical and electrostatic bonding, respectively.

Before examining the evidence on this point, it is profitable to consider the factors which promote the formation of complex compounds, with particular reference to ionic radii and the possibility of a transition between a purely electrostatic and a purely homopolar type of bonding.

An examination of the distribution amongst the metallic ions of the ability to form hydrates, ammoniates and stable complex salts shows at once that this tendency is greatest amongst metals of small ionic radius.

On Fajans' theory of ionic distortion, the maximum distorting effect is exerted by small cations of high ionic charge, acting on large, polarizable anions. Small size and high charge similarly promote complex formation, in which, in place of anions, polarizable dipolar molecules, such as ammonia or water, are subjected to the action of the central positive ion. Moreover, the firmness with which univalent negative ions are bound within the co-ordinated complex follows, in general, the order of their polarizabilities— $\text{Cl} < \text{Br} < \text{CN}$ and NO_2 .

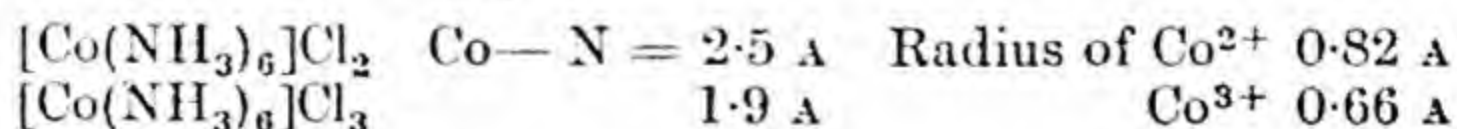
On the basis of Fajans' theory, one may therefore conceive of a co-ordinated complex as bound together, in the limiting case, by electrostatic forces. As the polarizing effect of the central cation increases, a state may be attained in which the mutual distortion is such that the electrostatic binding passes over into a covalent

linkage. We have this phenomenon illustrated by the multivalent metals, and particularly by cobalt, where the bivalent and trivalent states respectively exemplify the formation of the two types of complex. It is to be expected that the transition from one type to the other will be reflected in the chemical stability, optical properties, interatomic distances and other constitutive properties of the resulting compounds.

It must be pointed out, however, that the co-ordinating properties of ions are not determined solely by the ionic potential, which measures quantitatively the Fajans distorting effect. If this were so, the ability of the ferric ion to form complex ions would equal that of the cobaltic ion, while the aluminium ion should be the trivalent ion most given to the formation of complex compounds. Similarly, the cuprous ion should have as little ability as the sodium ion for complex formation. These are, in both cases, contrary to the chemical facts. It follows, therefore, that some additional specific factor must be involved, which confers on the metals of the transition series an ability to co-ordinate with neutral molecules or anions out of all proportion to their ionic potential. From the quantum mechanical theory of valency, it would appear that this factor is the availability of suitable electron orbits (usually d orbits) for the creation of strong, spatially directed, covalent bonds. We have discussed in Chapter II the concept of 'hybridization' of bonds, whereby a number of equivalent bonding orbitals could be produced; the evidence that bonds of this type are actually responsible for the formation of co-ordination compounds is discussed below.

(a) *Dimensional Evidence*.—Biltz and his school have shown that the molecular volumes of solid compounds at low temperatures can be treated as additive functions. The total molecular volumes of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_2$ and of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ are, however, practically identical, and evidence can be adduced that this is to be attributed to a contraction (*i.e.* a smaller effective molecular volume) of the ammonia in the luteocobaltic chloride. In the substituted cobalt-ammines, the amount of the contraction is less, but still appreciable.

The reason for the apparent contraction of ammonia in the luteocobaltic salt is revealed by the interatomic distances as measured by X-ray analysis:



It may be seen that there is a very considerable shortening of the $\text{Co}-\text{N}$ distance, which must imply the formation of a true chemical

bond between the two atoms. The Co—N distance in the hexamine cobaltic ion is, in fact, roughly equal to the sum of the covalent bond radii of cobalt and nitrogen.

(b) *Optical Evidence.*—The profound influence exerted by co-ordination upon the colour of salts shows at once that the attachment of co-ordinated groups modifies the electronic orbits of the central atom. It is well known that 'rare-gas-like' ions are colourless—i.e. have no selective absorption in the visible region. The coloured ions of the transition metals display a selective but weak absorption in the visible and near ultra-violet (as compared, for instance, with the very strong extinction of many dyestuffs), which is generally attributed to 'forbidden' transitions—i.e. to the relatively improbable excitation of electrons without change in their azimuthal quantum number. In the sharp spectra of the rare earths, these involve the screened $4f$ levels; with the transition metal ions the spectra are due to interaction with incompletely filled d levels which, on current views, are just the levels involved in co-ordination covalencies. Hence any rearrangement of these is likely to effect marked changes in the absorption spectra. The effect of stable co-ordination may be illustrated by comparing the red colour of the $[\text{Ni phenanthroline}_3]^{2+}$ ion, or the scarlet of nickel dimethyl glyoxime, with the light green of the dissociable $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ or $[\text{Ni}(\text{NH}_3)_6]^{2+}$ ions. Similarly, the pink hydrates and ammoniates of bivalent cobalt may be compared with the yellow colour of $[\text{Co}(\text{NH}_3)_6]^{3+}$ or $[\text{Co}(\text{NO}_2)_6]^{3-}$.

A second line of optical evidence is derived from the study of Raman spectra. The colour of many inorganic complex compounds makes it impossible to observe the characteristic frequency shifts involved in the Raman effect. Raman shifts have, however, been observed for a few compounds in solution—e.g. for the complex cyanides $\text{K}_3[\text{M}^{\text{III}}(\text{CN})_6]$ (where $\text{M} = \text{Co}, \text{Cr}$ or Rh) and for the ammines $[\text{Cu}(\text{NH}_3)_4]\text{X}_2$ and $[\text{Zn}(\text{NH}_3)_6]\text{X}_2$. They must be attributed to the characteristic vibrational frequencies of a covalent linkage. The magnitude of the shifts observed ($300\text{--}600\text{ cm.}^{-1}$) is distinctly less than that observed for typical single bonds.

(c) *Magnetic Evidence.*—In Chapter V it was seen that the presence of an unpaired electron in an atom or molecule must introduce a magnetic moment, and thus lead to paramagnetism. For the metals of the first transition series at least, Hund's maximum multiplicity principle was seen to be valid, so that the magnetic moments of the corresponding ions can be calculated from the resultant electronic spin. Conversely, any change in the ionic magnetic moment when complex compounds are formed must be associated with a change in the number of singly occupied electronic

orbits, and must imply that a rearrangement of electronic orbits has taken place.

If the susceptibilities of simple and complex salts of the transition metals are compared (Table 3), the striking fact is apparent that just those compounds of 6-co-ordinate trivalent cobalt and ferrous iron, and of 4-co-ordinate nickel, are diamagnetic which would, on general chemical grounds, be classed as penetration complexes. It is plain that, in these, the electrons formerly distributed amongst the $3d$ orbits according to Hund's principle have been completely paired up, and no other inference can be drawn than that the orbits so made available are used for the direct covalent binding of the co-ordinated groups or ions. A clear line of demarcation is thus drawn between these compounds and the chemically less stable 'normal' complex salts in which the full paramagnetism of the central ion is unchanged. In these there can be but little interaction between the electron systems of the attached groups and that of the central atom, and the bonding forces can therefore be regarded as chiefly or entirely electrostatic in character.

Table 3

Compound	μ_A , Bohr magnetons
FeCl_2	5.23
$[\text{Fe}(\text{NH}_3)_6]\text{Cl}_2$	5.25
$[\text{Fe dipyridyl}_3]\text{Cl}_2$	(Diamagnetic)
$\text{Fe}_2(\text{SO}_4)_3$	5.86
$\text{K}_3[\text{Fe}(\text{CN})_6]$	ca. 2
$\text{K}_4[\text{Fe}(\text{CN})_6]$	(Diamagnetic)
$\text{Fe}(\text{CO})_5$	(Diamagnetic)
CoCl_2	5.04
$[\text{Co}(\text{N}_2\text{H}_4)_2]\text{Cl}_2$	4.93
$[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$	(Diamagnetic)
$[\text{Co}(\text{NH}_3)_4\text{CO}_3]\text{Cl}$	(Diamagnetic)
$\text{Co}_2(\text{CO})_8$	(Diamagnetic)
NiCl_2	3.42
Ni dimethyl glyoxime	(Diamagnetic)
$\text{Ni}(\text{CO})_4$	(Diamagnetic)

The conception of co-ordination as an electrostatic phenomenon is probably applicable to all the hydrated cations (with the possible exception of the hexaquo chromic and cobaltic ions $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ and $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$, as is shown by the fair success of attempts by Magnus,¹⁰⁹ Garrick¹¹⁰ and others,¹¹¹ to calculate heats of hydration and stable co-ordination numbers on purely physical grounds. Even with the hydrates and loose ammoniates, however, the purely

¹⁰⁹ *Z. anorg. Chem.*, 1922, 124, 289.

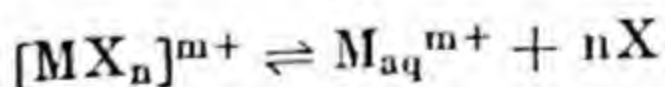
¹¹⁰ *Phil. Mag.*, 1930, [vii], 9, 131.

¹¹¹ *Cf. Bernal and Fowler, Trans. Faraday Soc.*, 1933, 29, 1049.

electrostatic binding probably represents only a limiting type, and it is likely that the co-ordinate link is in many cases a bond of 'fractional order', intermediate between a purely physical and a true chemical linkage.

(d) *Stereochemical Evidence*.—The stereochemistry of co-ordination compounds undoubtedly requires the assumption that they are formed by the operation of directed valency forces. The operation of electrostatic forces is necessarily undirected, so that the configuration taken up by any assemblage of particles so held together—for example, a hydrated metallic ion—must be dictated by symmetry, and will be due only to the mutual repulsion of the attached ions or dipoles. According as four or six groups are arranged around the central atom, so the whole will assume a tetrahedral or octohedral configuration. It has been seen, however, that around those atoms which form the most stable compounds of co-ordination number four the arrangement is not tetrahedral, but planar, and in this fact the operation of directed valency forces is implicit.

A further cogent argument is found in the stability of stereoisomers. In certain cases, the inter-transformation of stereoisomers during chemical reactions is known, but in general *cis* and *trans* series of both 6-co-ordinate and 4-co-ordinate compounds are quite stable and distinct. Moreover, optically active complex salts show, in many cases, little or no tendency for auto-racemization. That this should be the case, especially with planar 4-co-ordinate compounds, seems to imply, firstly, that the co-ordinate link has considerable *directional* properties, and secondly, that in solution the equilibrium



between the complex ions, the free central ion (really a hydrated ion, *i.e.* an aquo-complex) and the co-ordinating molecules or anions *X*, lies far over to the left-hand side. Only so can the stability of geometrical and optical isomers, towards isomerization or racemization, be explained. This stability has been most clearly exemplified in the behaviour of the tris-orthophenanthroline ruthenium salts. Dwyer and Gyarfas¹¹² have found that the optical isomers of the orange Ru^{II} salts, [Ru phenan₃]*X*₂, can be oxidized by ceric nitrate to the blue Ru^{III} compounds, [Ru phenan₃]*X*₃, without being racemized. Indeed, when the optically active Ru^{III} is reduced again, the original rotation of the Ru^{II} compound is restored.

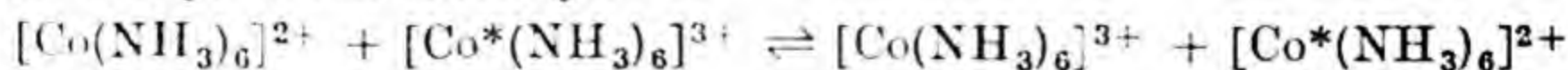
Isotope Exchange Experiments with Complex Salts.—If there is an equilibrium established in the solution of a complex

¹¹² *Nature*, 1949, 163, 918.

salt, after the manner of the general equation given above, it provides a mechanism whereby M atoms or ligand groups X might be exchanged between the complex ion and free M ions and X molecules (or anions) derived from the solution. Processes of this kind are generally undetectable, but by using isotopically 'labelled' ions—*e.g.* radioactive isotopes of the central ion M—their occurrence can be observed. The stability of a number of co-ordination complexes has, in fact, now been investigated from this standpoint. In general the results harmonize with deductions based on other evidence, but some features are conflicting.

Thus it was found ¹¹³ that ferrous ions exchanged at a measurable speed with the $[\text{Fe phenan}_3]^{2+}$ and $[\text{Fe dipy}_3]^{2+}$ ions—a result which seems at variance with the stability of the optical isomers of the same complexes towards racemization. Manganese acetylacetonate, $[\text{Mn acac}_2]$,¹¹⁴ zinc acetylacetonate, $[\text{Zn acac}_2]$, and other complex zinc compounds ¹¹⁵ have been found to undergo rapid exchange with the uncomplexed radioactive ions. In the pyridine solutions, used to dissolve the compounds for the exchange experiments, it is possible, however, that the chelate rings may have been opened, pyridine entering the complex. In that case, the results would not reflect the true stability of the complexes. In aqueous solutions of chromium complex salts, the system may be better defined; reaction occurs between the hexaquo-cation $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ and the complex under investigation. Menker and Garner ¹¹⁶ have shown that in these circumstances no detectable exchange takes place with the $[\text{Cr}(\text{CNS})_6]^{3-}$ or $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$ ions, in accordance with the optical stability of the latter compound. $[\text{Cr}(\text{CN})_6]^{3-}$, however, exchanges slowly, the time of half-change being about two days.

The behaviour of the hexammine cobaltic complex has been studied with especial thoroughness,¹¹⁷ and it has been shown that there is virtually no exchange, at the ordinary temperature, with other cobalt atoms present in solution as the $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ or the Co^{2+} aq cations. There is, however, a slow and measurable interchange (5 per cent complete in 400 hours) with the $[\text{Co}(\text{NH}_3)_6]^{2+}$ ion. This could be the result of a reversible dissociation, but it seems likely that the essential step, an electron transfer process, involves the complex ion directly:



¹¹³ Ruben, Kamen, Allen and Nahinsky, *J.A.C.S.*, 1942, **64**, 2297.

¹¹⁴ Drehmann, *Z. physikal. Chem.*, 1943, **B**, **53**, 227.

¹¹⁵ Leventhal and Garner, *J.A.C.S.*, 1949, **71**, 371.

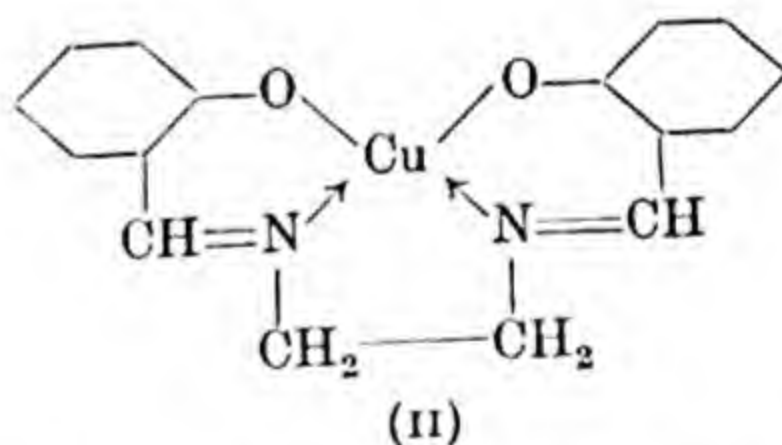
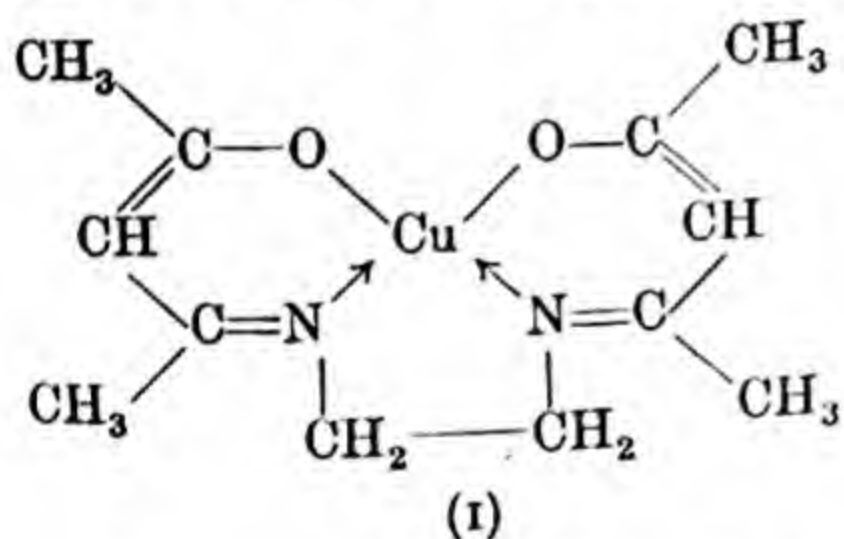
¹¹⁶ *J.A.C.S.*, 1949, **71**, 371.

¹¹⁷ S. A. Hoshowsky, O. G. Holmes and K. J. McCallum, *Can. J. Research*, 1949, **B**, **27**, 258.

Evidence favouring this view is to be found in the reported exchange of iron between the otherwise exceedingly stable $[\text{Fe}(\text{CN})_6]^{4-}$ and $[\text{Fe}(\text{CN})_6]^{3-}$ ions, and in the oxidation of the $[\text{Ru phenan}_3]^{2+}$ complex without loss of optical activity, referred to in a previous paragraph.

Experiments, in which the ligands have been indexed, have been carried out by studying the exchange between complex cyano-anions and the radioactive $^{14}\text{CN}'$ ion. There is practically no interchange with the complex iron cyanides, $[\text{Fe}(\text{CN})_6]^{3-}$ and $[\text{Fe}(\text{CN})_6]^{4-}$, and thus no detectable dissociation. With $[\text{Ag}(\text{CN})_2]'$ and $[\text{Ni}(\text{CN})_4]''$, the rate is believed to be faster than can be explained by the instability constants of these ions, which are known from electrometric measurements.

Calvin and Duffield¹¹⁸ consider that the velocity of isotope exchange, when carefully studied, affords a rather sensitive comparison of the co-ordinating power of different ligands with any one metal. Thus the rates of exchange of copper derivatives of salicylaldehyde ethylene diimine can be correlated with the reduction potentials of the complexes (*q.v.*, below). The subtle influences arising from modified resonance in the organic structures is indicated by the difference between (I) (time of half-change, $t_{\frac{1}{2}} = 37$ hours) and (II) ($t_{\frac{1}{2}} = 2.1$ hours).

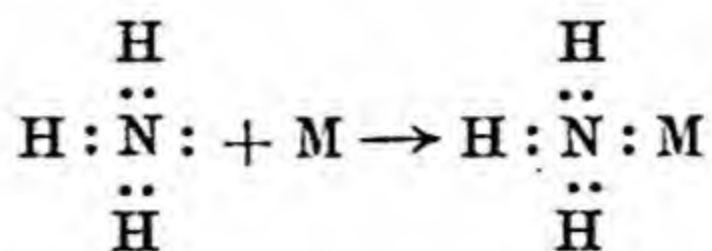


Theories of the Co-ordinate Linkage.—The first attempt to interpret co-ordination in terms of the electronic theory of valency was that of Sidgwick.¹¹⁹ The characteristic common to all molecules or ions capable of being co-ordinated to metallic atoms is the possession of at least one 'lone pair' of electrons, and a study of the polynuclear complex compounds shows that the number of co-ordinate links which may be formed by any one co-ordinating group is never greater than the number of 'lone pairs' available. Sidgwick therefore advanced the hypothesis that the co-ordinate link is a special case of the semi-polar type of bond, the

¹¹⁸ *J.A.C.S.*, 1946, 68, 557.

¹¹⁹ *Electronic Theory of Valency*, pp. 109 *et seq.*; 163 *et seq.*; 204 *et seq.*

co-ordinated group acting as the donor, and the central atom as acceptor :



The application of this theory proved fruitful. It appeared that the formation of the most stable complex compounds corresponded in certain cases to the acquirement by the central atom of the same 'effective atomic number' as the next inert gas, thus affording a plausible formal explanation of the stability and properties of such compounds. Thus, in hexammine cobaltic chloride and other cobaltamines, and in the ferrocyanide ion, we have :

$[\text{Co}(\text{NH}_3)_6]^{3+}$		$[\text{Fe}(\text{CN})_6]^{4-}$	
Co^{3+}	24 electrons	Fe^{2+}	24 electrons
6NH_3 donate	12	6CN^- donate	12
Total E.A.N.		Total E.A.N.	
36		36	

Moreover, as is discussed in Chapter XIV, the systematics of the interesting group of metallic carbonyls can be explained on the basis that the attainment of the 'inert gas configuration' confers stability on the compounds. It is especially striking that the compounds in which this condition is fulfilled are, without exception, diamagnetic.

That the attainment of this configuration is not the governing consideration is shown, however, by the fact that in the equally stable 4-co-ordinate compounds formed by nickel, platinum and gold, the effective atomic number is two short of that of the next inert gas ($\text{Kr} = 36$, $\text{Rn} = 86$) :

$\text{K}_2\text{Ni}(\text{CN})_4$		$\text{Pt}(\text{NH}_3)_2\text{Cl}_2$	
Ni^{2+}	26 electrons	Pt^{2+}	76 electrons
4CN^- donate	8	2NH_3 donate	4
		2Cl^- donate	4
Total E.A.N.		Total E.A.N.	
34		84	

KAuBr_4	
Au^{3+}	76 electrons
4Br^- donate	8
Total E.A.N.	
84	

These compounds are also diamagnetic. Sidgwick and Bose early sought to correlate the paramagnetism of complex ions with the difference between the effective atomic number of the metal atom (reckoned as in the examples above) and the inert gas number,

considering this difference as equal to the number of unpaired electrons. The Sidgwick-Bose rule, which is tantamount to the assumption of the Hund multiplicity principle, gives correct results for the complex salts of copper, chromium, and 6-co-ordinate nickel, but special *ad hoc* hypotheses must be introduced to explain the diamagnetism of the planar 4-co-ordinate compounds just considered. The successful application of the rule may be illustrated by the following examples:

$[\text{Cu}(\text{NH}_3)_4]^{2+}$
 Cu^{2+} . . . 27 electrons
 4 NH_3 donate 8

—
 Total E.A.N. 35

36 — E.A.N. = 1 unpaired electron

$\mu_{\text{calc.}}$ 1.73 Bohr magnetons

μ_{found} 1.82

$[\text{Ni dipyridyl}_3]^{2+}$
 Ni^{2+} . . . 26 electrons
 3 dipyridyl . 12

—
 Total E.A.N. 38

E.A.N. — 36 = 2 unpaired electrons

$\mu_{\text{calc.}}$ 2.83 Bohr magnetons

μ_{found} ca. 2.8

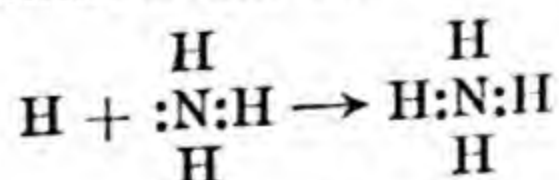
While the condition for stability and diamagnetism of complex compounds is clearly the building up of some closed electronic shell, the attainment of the inert gas number, as such, cannot be taken as the essential criterion. That this is the case follows also from the equivalence of the co-ordinate links; in building up from, *e.g.*, the Co^{3+} ion to a krypton-like atom there are not orbits for twelve completely equivalent electrons.

Two other objections have been brought against the simple electron-pair bond theory outlined above.

(a) It involves an improbable accumulation of negative charge on the central atom. Thus, in the $[\text{Co}(\text{NH}_3)_6]^{3+}$ ion, the nett charge upon the cobalt atom is $+3 - 6 = -3$ units, while each NH_3 has an effective charge of $+1$ unit.

(b) The 'lone pair' of electrons possessed by water, ammonia and other neutral co-ordinating groups, represented as responsible for the formation of the co-ordinate linkage, is the $2s^2$ pair. A completed sub-level such as this has no bonding properties, and so could not form the supposed link.¹²⁰ To excite one electron of the s^2 pair would, however, require a high energy, and so cannot readily be invoked as the first step in the act of co-ordination.

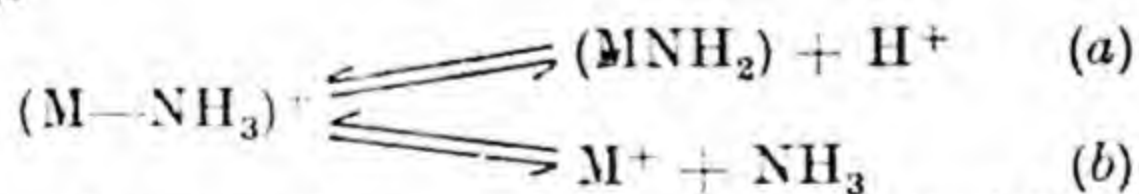
The answer to the second objection may be perceived from a consideration of the simplest possible case of co-ordination, namely, the formation of the ammonium ion:



The completed ammonium ion is iso-electronic with methane, and

¹²⁰ Hunter and Samuel, *J.C.S.*, 1934, 1180; *Chem. and Ind.*, 1935, 635.

undoubtedly has the same structure. The hydrogen atoms are completely equivalent, and all distinction between the original s and p electrons of the nitrogen or carbon atom, respectively, has disappeared. Each orbit partakes of the s and three p orbits originally present, so that four hybrid $[sp^3]$ orbits are formed. These can each accommodate a pair of electrons shared with one hydrogen atom, so that four completely equivalent bonds result. This view, generally accepted for the case of methane, must be valid also for ammonium, but the case of the co-ordination of ammonia to a metallic ion instead of to a hydrogen ion is, in principle, exactly similar. Here, again, it is not the direct donation of the $2s^2$ electron pair which is involved, but rather the reorganization of the levels of the nitrogen atom to form $[sp^3]$ hybrid bonds. The valence angles in the NH_3 and H_2O molecules are considerably larger than the 90° angle between the axes of the p electron wave functions. As has been pointed out by Coulson, this may be only partly attributable to the repulsion between the hydrogen atoms; an alternative view is that in these molecules at least a partial hybridization of $2s$ and $2p$ orbits has already taken place. The lone pair of electrons is, then, not an s^2 pair; its wave function already has something of the directional properties needed to form a bond with good 'overlap', and the promotion of one electron need no longer be regarded as the necessary preliminary step in co-ordinate link formation. Owing to the different electron affinities of the metallic ion and of hydrogen, the $[sp^3]$ bonds will no longer be equivalent. With ions of high electron affinity—*e.g.* heavy ions of high valency, such as Pt^{4+} —the strength of the metal-nitrogen bond may so far outweigh the strength of the hydrogen-nitrogen bonds, that the dissociation into metal amide and hydrogen ion (*a*) proceeds more readily than dissociation into metal ion and ammonia (*b*).



Pauling has developed on quantum mechanical lines a theory of the complex compounds of the transition metals which amounts to a development of Sidgwick's electron pair bond theory.¹²¹ In the heavier atoms, as was seen in Chapter II, a certain overlapping of energy levels takes place between the different principal quantum groups. In the first transition series, for example, the $4s^2$ levels become filled before any of the $3d$ levels, and the variable valency of the transition metals shows that the $3d$ and $4s$ levels can differ little in energy. Where such a state exists, the normal quantization

¹²¹ *J. Amer. Chem. Soc.*, 1931, 53, 1367, 3225.

can, on Pauling's view, be broken down, and new hybrid orbits can be formed. It is possible in this way to obtain four or six equivalent orbits, according to the number of vacant orbits available for hybridization.

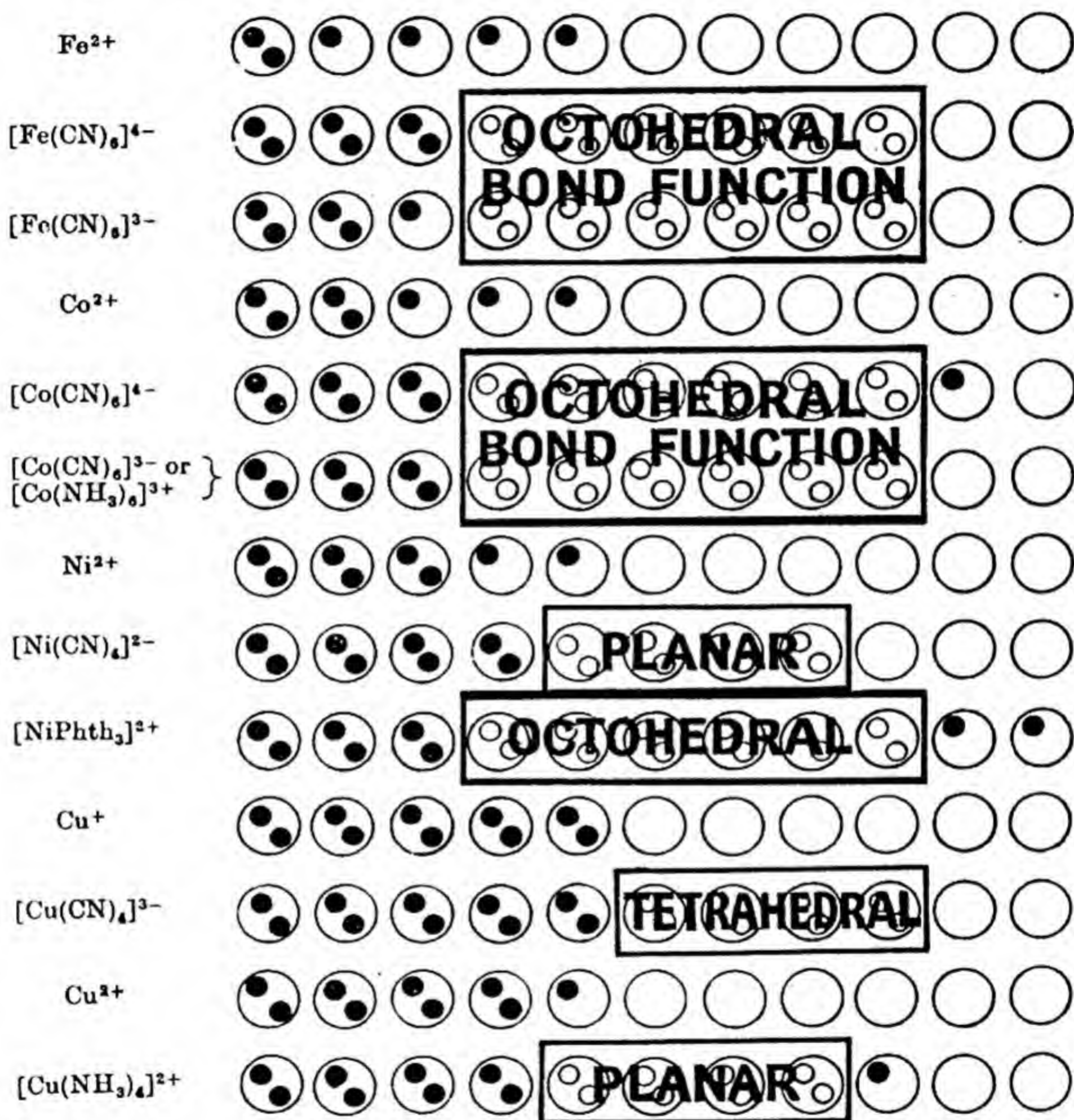
In the first transition series, at least, the Hund rule of maximum multiplicity is followed—*i.e.* as many orbits as possible are occupied singly before any pairing of electrons takes place. The striking change from paramagnetism to diamagnetism when complex ion formation occurs shows that the process involves the redistribution of electrons so that pairing takes place throughout. In this way, some orbits are vacated and made available for hybridization.

Pauling found that, with six bond functions available—two *d*, one *s* and three *p* bond functions—six new equivalent orbits can be formed, directed to the apices of a regular octohedron. With four bond functions, two distinct configurations can be produced, depending on the symmetry properties of the orbits taken. From three *d* and one *s* orbit, or three *p* and one *s* orbit, four equivalent bonds arranged tetrahedrally may be made. If, however, there is one *d* orbit available, this can be combined with one *s* and two *p* orbits to give four new coplanar bonds, directed towards the corners of a square. Each of the new orbits formed in any of these ways can accommodate two electrons, which—in terms of the Sidgwick theory—may be obtained by sharing either with a negative ion, such as CN^- , or with the 'lone pair' of a neutral molecule, such as ammonia. It is especially noteworthy that each of the sets of hybrid orbits represents a closed configuration, so that if the levels below the hybridized complex-forming orbits are all completely filled, the resulting complex must necessarily be diamagnetic. In this way Pauling predicted the diamagnetism of 4-co-ordinate nickel.

The application of this theory shows it to explain the experimental facts fairly well, as may be seen from Fig. 30. If, in the ferrous ion, the electrons be paired up completely in the three lowest *d* levels, two *d* orbits are made available for combination with the 4*s* and 4*p* orbits. Six new octohedrally-arranged bonds can then be formed, and will give rise, as can be seen, to a completely closed configuration. Hence, the $[\text{Fe}(\text{CN})_6]^{4-}$ ion is diamagnetic. The ferric ion has one electron less to start with, so that the complex ion resulting from the same process must be paramagnetic, and should have $\mu_A = 1.73$ Bohr magnetons; the experimental figure for $\text{K}_3[\text{Fe}(\text{CN})_6]$ is about 2 Bohr magnetons, implying that orbital angular momentum makes a small contribution.

Trivalent cobalt will be analogous to ferrous iron, but the case of the cobaltous compounds is particularly interesting. Here, in

order to make two d orbitals available, one electron must be promoted to a higher ($5s$) level. It may be expected, therefore, that this promoted electron would readily be ionized off—*i.e.* that the true complex compounds of bivalent cobalt would readily be oxidized



● Occupied electronic orbit ○ Unoccupied electronic orbit

FIG. 30.

to the trivalent state. This is borne out by the strong reducing properties of $\text{K}_4[\text{Co}(\text{CN})_6]$, and by the large shift in the oxidation-reduction potential of cobalt in ammoniacal solutions. This conception of the promotion of electrons to make orbitals available is, in some respects, a drawback to the theory, since it might similarly

be expected that nickel in its 6-co-ordinate complexes would be easily oxidized to the quadrivalent state. This is, of course, not the case, although the paramagnetism of $[\text{Ni dipyridyl}_3]\text{Cl}_2$ shows it to have the two unpaired electrons predicted. With platinum, where the same rearrangement of the $5d$, $6s$ and $6p$ orbits takes place, 6-co-ordination is rare in platinous compounds, and is usually associated with the expected oxidation to quadrivalency.

In the case of 4-co-ordinate compounds, it may be seen that by pairing up the d levels of Ni^{2+} , one d orbit is made available for the formation of a planar diamagnetic complex. With Cu^{2+} the same rearrangement may be made by promoting one electron (although trivalent copper is unknown—see preceding paragraph—trivalent gold is found, as Gibson has pointed out, only in planar 4-co-ordinate complexes). The planar cupric complex still has one unpaired electron, and so is paramagnetic.

The cuprous ion Cu^+ and zinc ion Zn^{2+} , which are iso-electronic, both have their $3d$ levels filled. They can therefore hybridize only $4s$ and $4p$ orbits, and must form tetrahedral diamagnetic 4-co-ordinate complexes. Moreover, since the neutral nickel atom (in the state $3d^{10}$) is iso-electronic with Cu^+ and Zn^{2+} , nickel carbonyl, Ni(CO)_4 , should be iso-electronic with the $[\text{Zn(CN)}_4]^{2-}$ ion. Its structure should therefore be tetrahedral, as was found to be the case.

Finally, in the Cr^{6+} ion, the $3d$ level is completely empty. For the formation of bonds, the lowest orbits available for hybridization are $3d$ and $4s$, so that $[sd^3]$ hybridization takes place; derivatives of sexavalent chromium, such as the chromate ion CrO_4^{2-} , therefore have a tetrahedral configuration.

The relation of the bonding electrons in co-ordination compounds to the quantization of the central atom can thus be formulated in a manner not inconsistent with the quantum mechanical theory of valency. Nevertheless, the theory is not yet complete, and does not account satisfactorily for the formation and unusual properties of certain groups of co-ordination compounds. These include, for example, the complexes formed by olefins, *e.g.* $[\text{PtCl}_2.\text{C}_2\text{H}_4]_2$,¹²² $\text{K}[\text{PtCl}_3.\text{C}_6\text{H}_5\text{CH:CH}_2]$,¹²³ by carbon monoxide—*e.g.* $[\text{PtCl}_2.\text{CO}]_2$ and the metal carbonyls (see Chap. XIV)—and by PF_3 —*e.g.* $[\text{PtCl}_2(\text{PF}_3)_2]$.¹²⁴ For the co-ordination of molecules such as NH_3 , no mechanism is possible other than the formation of a σ -bond with the lone pair of electrons. Chatt has suggested, however, that

¹²² Anderson, *J.C.S.*, 1934, 971 ; Chatt and Hart, *Chemistry and Industry*, 1949, 146 ; Hel'man, 'Complex Compounds of Platinum with Unsaturated Molecules', *Soviet Acad. Sci.*, 1945.

¹²³ Anderson, *J.C.S.*, 1936, 1042.

¹²⁴ J. Chatt, *Nature*, 1950, 165, 637.

with the special groups mentioned (and possibly more widely), some kind of a π -type dative bond may be formed, involving interaction between filled d orbitals of the metal atom and empty d orbitals of the attached molecule (as with PF_3), or between d orbitals of the metal and π -bonds already existing in the ligands.

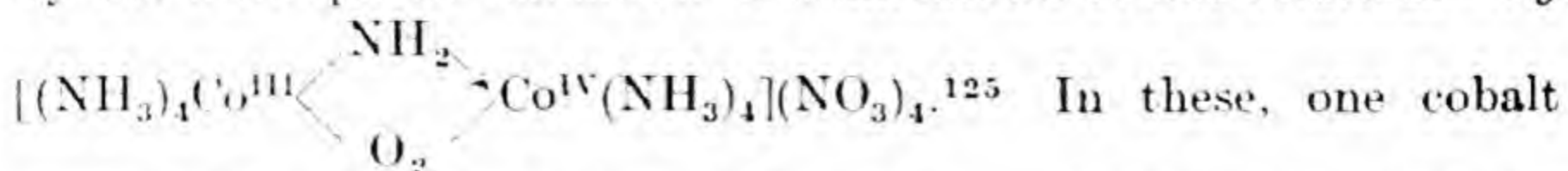
The theory of co-ordination is therefore still in a state of development. Quite apart, however, from the validity or falsity of current interpretations of the chemical bond, the concept of complex formation has its own value, for as was perceived by Werner, it has a wide scope as a unifying principle throughout inorganic chemistry. This aspect of the matter is emphasized in relation to a few special topics in the remaining sections of this chapter.

The Stabilization of Valency States by Complex Formation.

A particularly interesting aspect of complex formation is the manner in which the attachment of strongly co-ordinating groups may lead to the stabilization of a valency state, derivatives of which are otherwise unstable; *i.e.* the oxidation-reduction potentials may be profoundly modified.

Cobalt.—A familiar and striking example of this phenomenon is found in the cobaltammines. Cobalt may be oxidized to the trivalent state electrolytically, and then forms the sulphate $\text{Co}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ and the alums—*e.g.* $\text{CsCo}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ —which are very unstable. The fluoride CoF_3 has also been obtained. All these compounds have strong oxidizing tendencies, however, due to the readiness with which the cobalt reverts to the bivalent state. In the presence of ammonia, the relative stabilities of the $[\text{Co}(\text{NH}_3)_6]^{3+}$ and $[\text{Co}(\text{NH}_3)_6]^{2+}$ ions are so far reversed that oxidation to the former state is effected by atmospheric oxygen at room temperature. The same stabilizing effect is produced by the co-ordination of anions, as is shown by the strong reducing properties of potassium cobaltocyanide. The quantitative magnitude of the effect is shown by the large displacement of the oxidation-reduction potential.

The stabilization of the higher valencies of cobalt by complex formation is such that the existence of quadrivalent cobalt compounds becomes possible, and a number of such derivatives are known among the μ -peroxo polynuclear cobaltammines obtained by the atmospheric oxidation of ammoniacal cobalt solutions—*e.g.*



atom is formally trivalent, and the other quadrivalent; as in other

¹²⁵ Werner, *Annalen*, 1910, 375, 15.

such cases, it may be assumed that the states of the two atoms become equivalent by a resonance process, and the compounds are marked by their deep colours.

Nickel.—From the discussion of the nature of the co-ordinate bond given in a previous section, it may be seen that the stability of the 6-co-ordinate compounds of Co(iii) is connected with the filling of all electron levels up to and including the octohedral hybrid orbitals used in forming the co-ordination complex. With nickel, valence states both higher and lower than the usual bivalent state may be stabilized in the same way. Compounds of formally *univalent* and *zero-valent* nickel both exist in the form of complex cyano-anions. When $K_2[Ni(CN)_4]$ is reduced with sodium amalgam, a red solution is obtained, which was shown by Belucci and Corelli¹²⁶ to contain univalent nickel, though the compound $K_2[Ni(CN)_3]$ has only recently been obtained in the pure state.¹²⁷ This complex salt is relatively stable, although very sensitive towards oxidation. The simple (or perhaps autocomplex) cyanide NiCN, obtained by acidifying its solution, disproportionates, however, into nickel and nickel (ii) cyanide. It is noteworthy that $K_2[Ni(CN)_3]$ is diamagnetic,¹²⁸ though it is not known whether the compound involves bivalent nickel, with a Ni-Ni bond, or whether nickel is actually present in two diamagnetic valence states, as $Ni(ii) + Ni(0)$. It has, indeed, been found¹²⁷ that, in liquid ammonia solutions, reduction can proceed further, to yield $K_4[Ni(CN)_4]$, which is clearly derived from formally zero-valent nickel: this formal valence state is present also in nickel carbonyl, $Ni(CO)_4$ (see Chap. XIV), which has long been known. The $[Ni^0(CN)_4]^{4-}$ anion must have the CN^- groups bound by $[sp^3]$ hybrid orbitals, outside a complete M shell. As such, it is iso-electronic with the $[Zn(CN)_4]^{2-}$ anion, and undoubtedly has a tetrahedral configuration, in contrast with the planar 4-co-ordinate compounds of Ni(ii)—e.g. $[Ni(CN)_4]^{2-}$.

Trivalent nickel, as has already been mentioned (p. 138), is so far stabilized in suitable complex compounds that $[NiBr_3(Et_3P)_2]$ is formed directly by the action of bromine on $[NiBr_2(Et_3P)_2]$.^{128a}

Bivalent nickel, as has been stated, forms stable 4-co-ordinate planar complexes, involving $[dsp^2]$ orbitals, whereas six-co-ordinate complexes would involve the promotion of two electrons to higher levels. With the homologous elements platinum and palladium, the effect of this is to stabilize the quadrivalent state of the element in 6-co-ordinate complexes, which then involve the electron con-

¹²⁶ *Atti R. Acad. Lincei*, 1913, 22, 485; *Gazzetta*, 1919, 49, ii, 70.

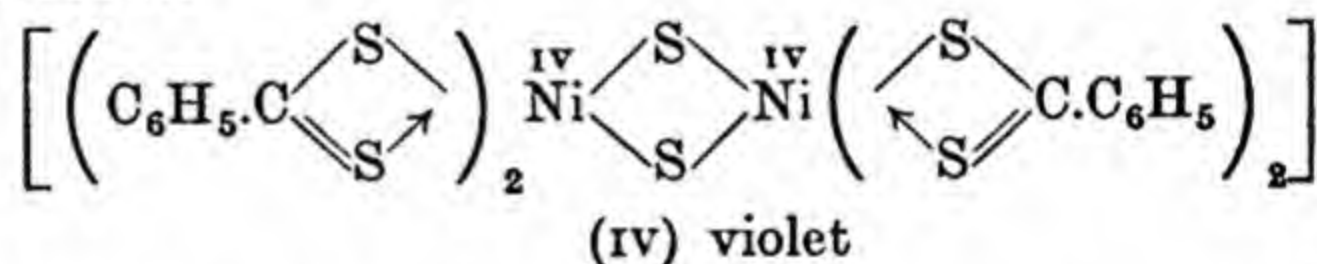
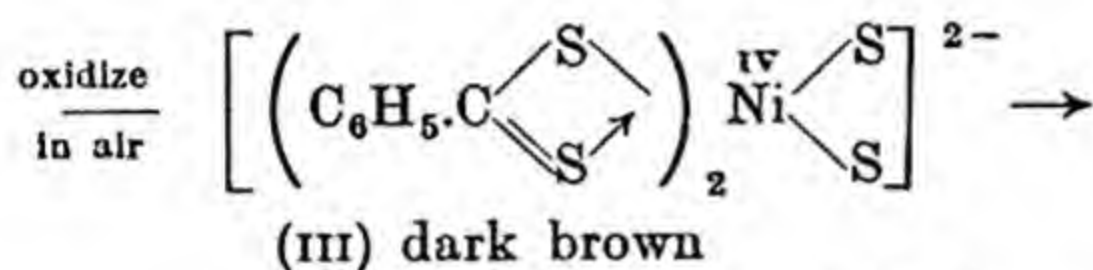
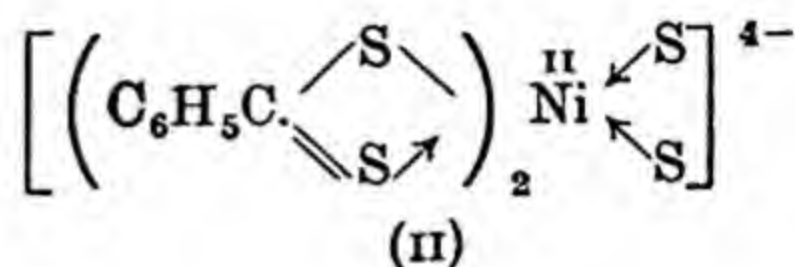
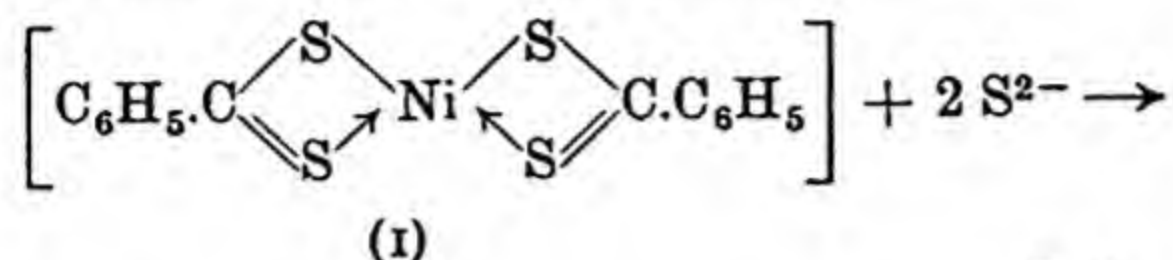
¹²⁷ J. N. Eastes and W. M. Burgess, *J. Amer. Chem. Soc.*, 1942, 64, 1187.

¹²⁸ D. P. Mellor and D. P. Craig, *J. Proc. Roy. Soc., N.S.W.*, 1943, 76, 281.

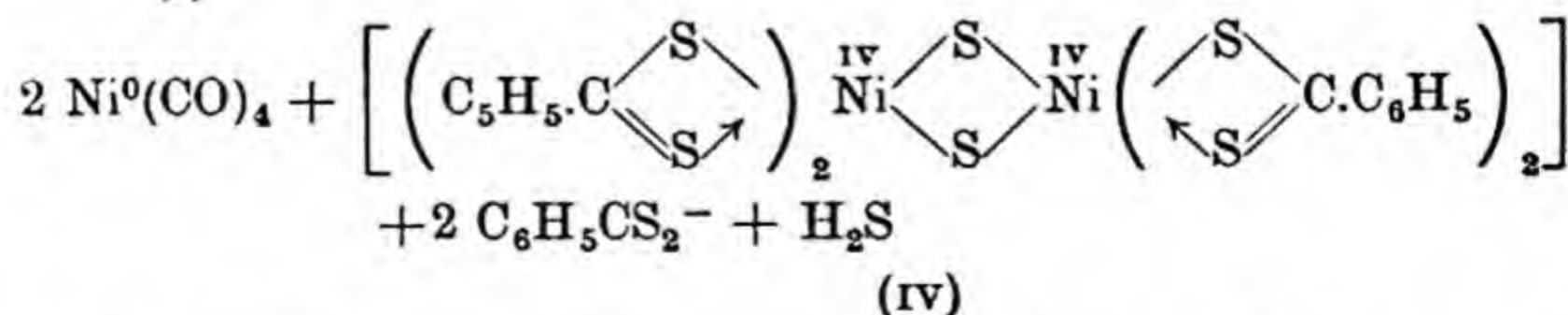
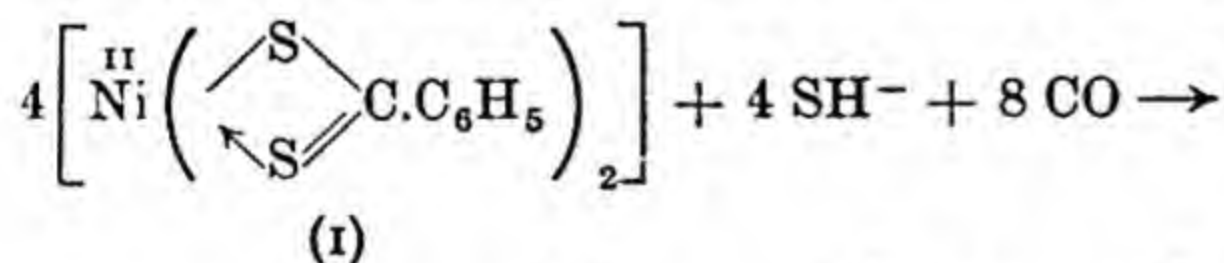
^{128a} K. A. Jensen and B. Nygaard, *Acta Chem. Scand.*, 1949, 3, 474.

configuration $d^6[d^2sp^3]^2$. Quite recently ¹²⁹ it has been found that ligands with a strong enough tendency to form covalent bonds with nickel can similarly give rise to stable co-ordination compounds of Ni^{IV} .

This is the case with organic thio-acids and similar compounds. Thus $\text{Ni}(\text{S.CS.C}_6\text{H}_5)_2$ is readily oxidized in a strongly alkaline solution containing sulphide ions.



The anionic complex (II) of Ni^{II} readily parts with its promoted electrons, forming an anionic complex (III) containing Ni^{IV} . In the absence of an external electron-acceptor, and in presence of groups which can stabilize zero-valent nickel (*e.g.* carbon monoxide), (II) undergoes an internal oxidation-reduction process: *e.g.*

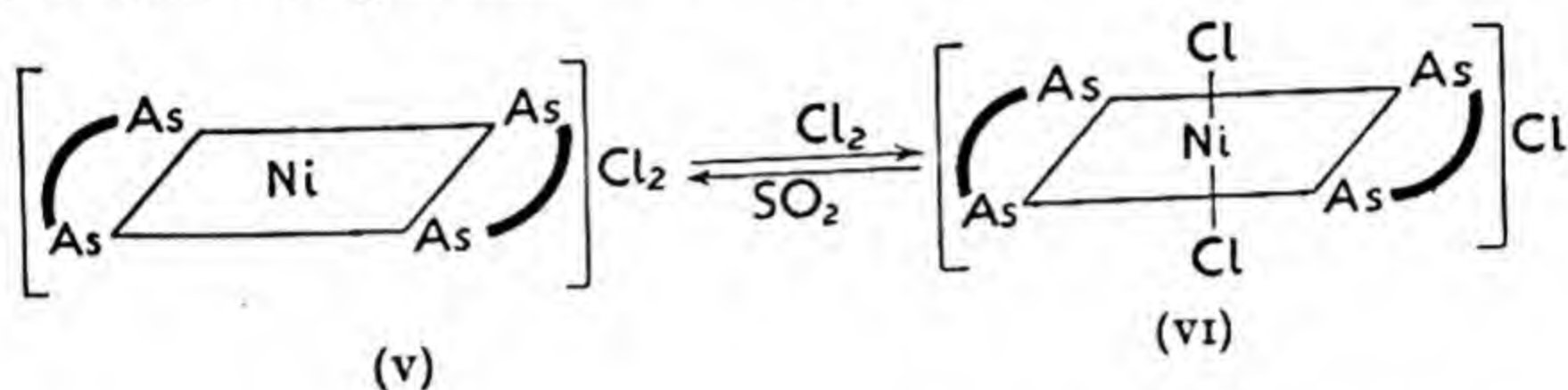


Nyholm ^{129a} has found a similar stabilization of Ni^{IV} by chelation with di-tertiary arsines. Thus $o\text{-(CH}_3)_2\text{As.C}_6\text{H}_4\text{.As(CH}_3)_2$ readily

¹²⁹ W. Hieber and R. Brück, *Naturwiss.*, 1949, 36, 312.

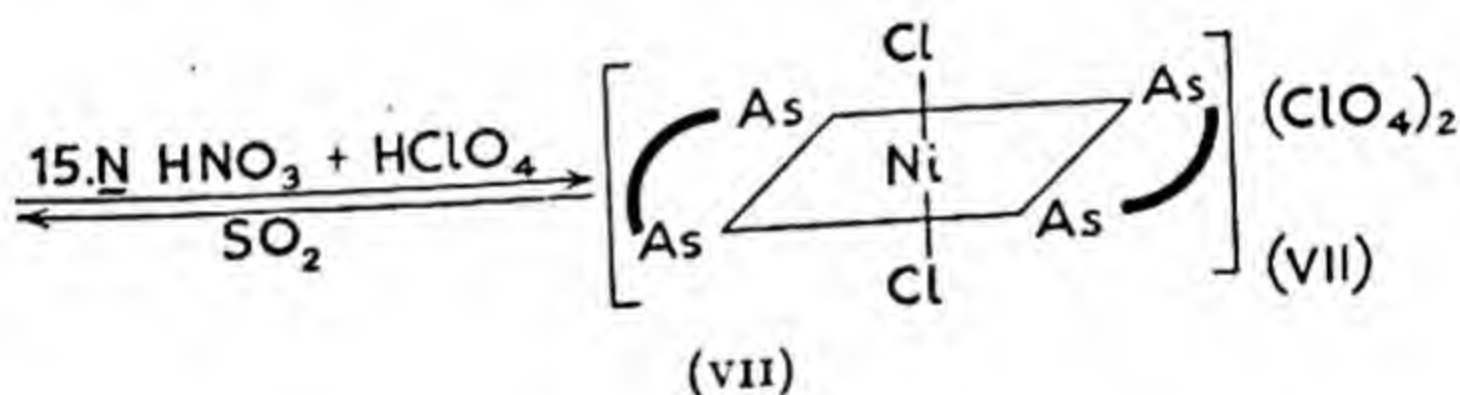
^{129a} *J.C.S.*, 1951, 1767.

combines with nickel-(ii), forming the red, diamagnetic, planar complex salts $[\text{Ni}(\text{diars})_2]\text{X}_2$. The chloride of this series (V) can be oxidized by chlorine to a yellow-brown compound which—in contrast with Jensen's Ni^{III} derivatives—is shown by its mode of ionization and its magnetic susceptibility to be an octohedral complex of Ni^{III} , (VI). This in turn can be converted by sufficiently strong oxidants to deep blue-green compounds which have the correct composition, ease of reduction and diamagnetism expected for a compound of quadrivalent nickel (VII), with the same electronic configuration as the complex compounds of cobalt-(iii).



Ni^{II}
Red, diamagnetic
[dsp²] bonds

Ni^{III}
Yellow-brown, $\mu = 1.89$
[d²sp³] bonds + 1 unpaired
promoted electron



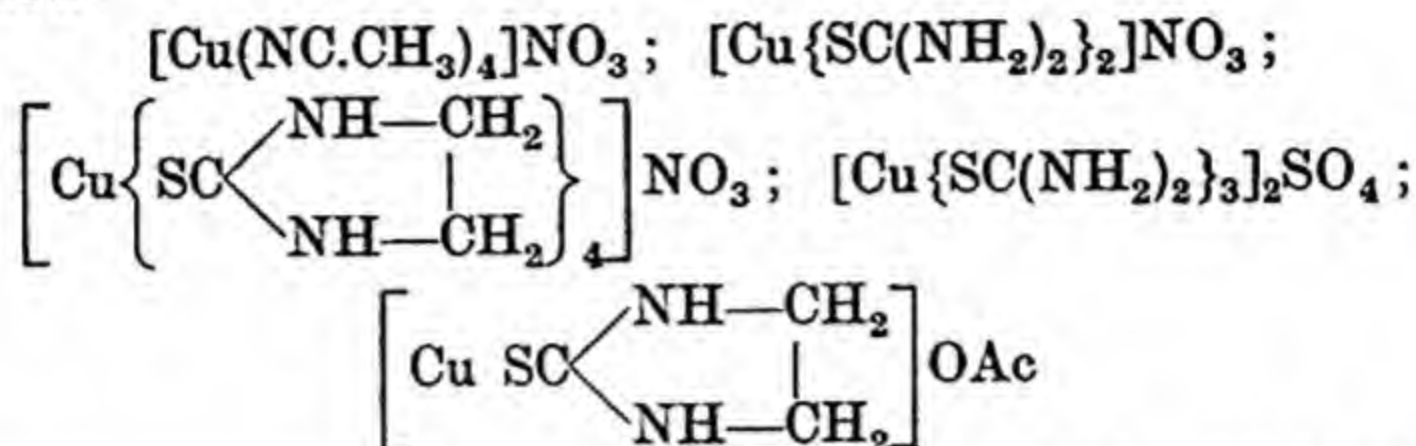
Ni^{IV}
Deep blue-green, diamagnetic
[d²sp³] bonds

Copper.—Both higher and lower valency states may be stabilized by appropriate co-ordinating groups. Thus, the instability of cupric iodide and cupric cyanide is a familiar fact which finds application in analysis. The iodide $[\text{Cu en}_2]\text{I}_2 \cdot 1 \text{ or } 2\text{H}_2\text{O}$ is stable, however, with no tendency to revert to the cuprous state.¹³⁰ In the case of the corresponding cyanide, stabilization of the bivalent state is not so complete, so that a derivative of both bivalent and univalent copper, $[\text{Cu en}_2][\text{Cu}(\text{CN})_2]_2$, is obtained; its formation may be attributed to the competing effect of the stabilization of the cuprous state in the complex anion. In the same way, the $[\text{Cu en}_2]$

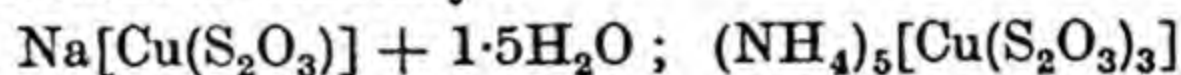
¹³⁰ G. T. Morgan and Burstall, *J.C.S.*, 1926, 2018, 2027; 1927, 1259.

cation is not reducible by hypophosphites (compare the reducibility of the cupric ion), but forms a stable salt $[\text{Cu en}_2](\text{H}_2\text{PO}_2)_2$.

The co-ordination of acetonitrile,¹³¹ thiocarbamide,¹³² or ethylene thiocarbamide,¹³³ similarly stabilizes the cuprous state, so that the nitrates, sulphates and acetates of the complex cuprous ions may be formed:



The complex cuprous thiosulphates,¹³⁴ in which—as in the thiocarbamide compounds—copper is co-ordinated to sulphur, also possess considerable stability:



Silver.—Univalent silver is also stabilized by co-ordination with sulphur compounds, in the sense that the complexes with ethylene thiocarbamide (abbreviated *etu*) yield a chloride and bromide, $[\text{Ag etu}_3]\text{Cl}$, $[\text{Ag etu}_2]\text{Br}$, which are not photosensitive.¹³⁴ The bivalent state is readily stabilized by co-ordination, especially with pyridine derivatives. Barbieri¹³⁵ in 1912 obtained $[\text{Ag}(\text{pyr})_4]\text{S}_2\text{O}_8$ by the oxidation of silver nitrate with persulphate in the presence of pyridine, while the corresponding nitrate may be prepared by electrolytic oxidation. The complex argentic cations containing *o*-phenanthroline¹³⁶ and dipyridyl,¹³⁷ $[\text{Ag phth}_2]^{2+}$ and $[\text{Ag dipy}_2]^{2+}$, are very stable, and numerous salts of these cations have been prepared. Reference has already been made (p. 139) to an inner complex salt, argentic picolinate, which has been shown to have a planar configuration.

Manganese.—The reduction of alkali manganocyanides with aluminium (or Devarda's alloy) and caustic alkali yields derivatives of univalent manganese, $\text{R}_5[\text{Mn}(\text{CN})_6]$.

Tervalent manganese is unstable in the halides MnF_3 , MnCl_3 .¹³⁸

¹³¹ H. H. Morgan, *ibid.*, 1923, 2901.

¹³² Rosenheim and Loewenstamm, *Z. anorg. Chem.*, 1903, 34, 62; Kohnschütter, *Ber.*, 1903, 36, 1151; *Annalen*, 1906, 349, 232.

¹³³ Morgan and Burstall, *J.C.S.*, 1928, 143.

¹³⁴ Spacu and Murgulescu, *Chem. Zentr.*, 1930, i, 3422; ii, 535; 1931, i, 1426.

¹³⁵ Barbieri, *Gazzetta*, 1912, 42, 7; *Ber.*, 1927, 60, 2424.

¹³⁶ Hieber and Mühlbauer, *Ber.*, 1928, 61, 2149.

¹³⁷ Sugden, *J.C.S.*, 1932, 161.

¹³⁸ Křepelka and Kubis *Coll. Czech Chem. Comm.* 1935 7, 105.

and in the red alums $\text{RMn}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, but it is noteworthy that acetylacetone forms an inner-complex salt only with tervalent manganese.¹³⁹ An analogy is found in iron, which also combines with β -diketones in the ferric state only. Tervalent manganese is stabilized also in the manganicyanides, $\text{R}_3[\text{Mn}(\text{CN})_6]$, the most stable of the three complex cyanides of manganese.

Iron.—The ferrous state, which in simple salts is readily oxidized by atmospheric oxygen, is strongly stabilized by co-ordination with dipyridyl or *o*-phenanthroline, so that the salts $[\text{Fe phth}_3]\text{X}_2$, $[\text{Fe dipy}_3]\text{X}_2$, are much more stable than the ferric compounds,¹⁴⁰ and find application as redox indicators in oxidimetric titrations. The magnitude of the displacement of the ferrous/ferric oxidation-reduction potential in a few complex compounds is shown by the appended table. The remarkably selective action of co-ordinating groups is demonstrated, however, in that the chelating groups α -pyridyl hydrazine¹⁴¹ (I) and α -pyridyl pyrrole¹⁴² (II) are stated to favour the stability of the ferric state, as also do the β -diketones.

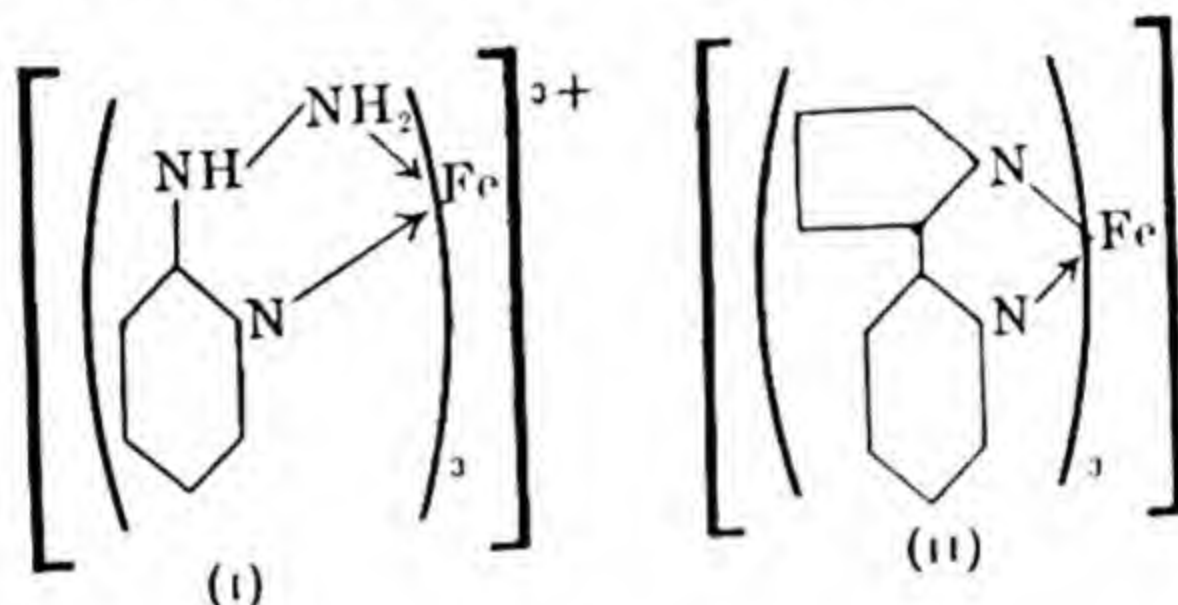


Table 4

Equilibrium	Oxidation-reduction potential (British Convention)
$\text{Co}^{2+}/\text{Co}^{3+}$	+ 1.8 volts
$[\text{Co}(\text{CN})_6]^{4-}/[\text{Co}(\text{CN})_6]^{3-}$	- 0.8 „
$\text{Fe}^{2+}/\text{Fe}^{3+}$	+ 0.74 „
$[\text{Fe}(\text{CN})_6]^{4-}/[\text{Fe}(\text{CN})_6]^{3-}$	+ 0.49 „
$[\text{Fe phth}_3]^{2+}/[\text{Fe phth}_3]^{3+}$	+ 1.14 „
$[\text{Fe dipy}_3]^{2+}/[\text{Fe dipy}_3]^{3+}$	ca. + 1.1 „
$[\text{Fe nitro-phth}_3]^{2+}/[\text{Fe nitro-phth}_3]^{3+}$	+ 1.25 „

¹³⁹ Urbain and Debierne, *Compt. rend.*, 1899, 129, 302.

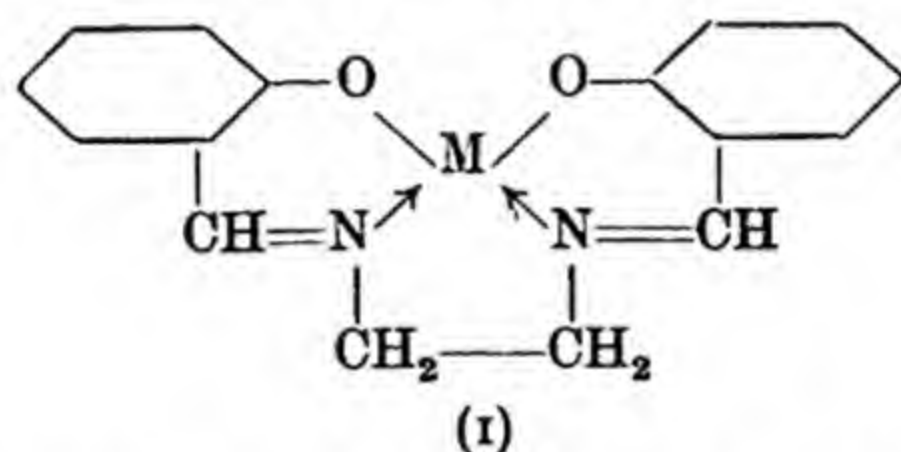
¹⁴⁰ Blau, *Monatsh.*, 1898, 19, 647; Hammett and Walden, *J. Amer. Chem. Soc.*, 1933, 55, 2649; 1936, 58, 1668; Simon and Haufe, *Z. anorg. Chem.*, 1936, 230, 160.

¹⁴¹ Emmert and Schneider, *Ber.*, 1933, 66, 1875.

¹⁴² Emmert and Brandt, *ibid.*, 1927, 60, 2211.

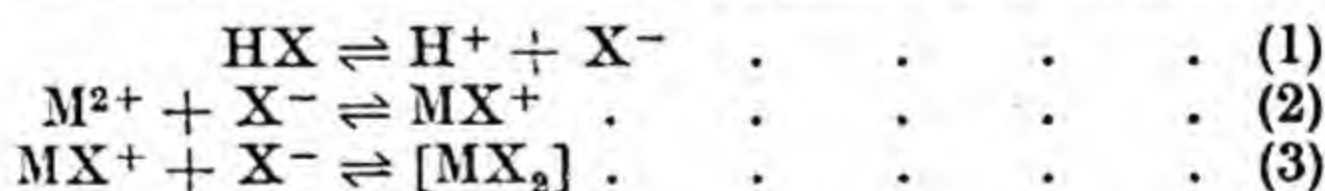
The Stability of Complex Salts.—Within recent years, a number of workers have attempted to ascertain the factors that determine the stability of the co-ordinated complex, and the way in which the stability changes as either the central atom or the ligands are altered.

Pfeiffer, Thielert and Glaser ¹⁴³ obtained some qualitative information from a study of the displacement of the bivalent metallic ion M_A^{2+} from inner complex salts with bis-salicylaldehyde ethylene diimine (*e.g.* (I)) by another bivalent ion M_B^{2+} . Such reactions, which, because of the sparing solubility of these compounds in water, are necessarily carried out in solvent (such as pyridine), which themselves exert a strong solvating power, are really exchange reactions, not simple displacement reactions:



The position of equilibrium therefore involves the relative stability both of the $[M \text{ pyr}_6]^{2+}$ and the $[M \text{ sal-en}_3]$ complexes, but Pfeiffer concluded that the sequence of stability of the inner complex salts was $\text{Cu}^{II} > \text{Ni}^{II} > \text{Fe}^{III} > \text{Zn}^{II} > \text{Mg}^{II}$, an order confirmed by more recent work.

A more quantitative approach to the problem emerges from a consideration of the successive equilibria involved in the formation of an inner complex salt, such as the complex (I) just mentioned. If we denote by HX one equivalent of the complex-forming molecule, we have in the solution the successive reactions



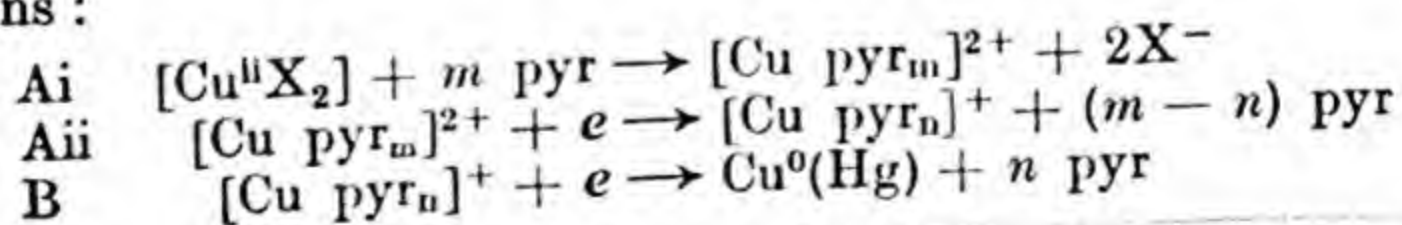
There is, in effect, competition between the H^+ and M^{2+} ions (or MX^+) for combination with the anions X^- . If hydrogen ions are removed from solution, by neutralization, the buffering action of the X^- —HX system is substantially modified, through the removal of X^- ions in reactions (2) and (3). It is, in fact, possible to carry out a potentiometric titration of a system containing known concentrations of the metal ion M^{2+} , the complexing agent HX and excess free acid, and to determine from the course of the neutralization

¹⁴³ *J. prakt. Chem.*, 1939, 152, 145.

curve the precise manner in which the concentration of X^- ions bound in the complex salt changes during the neutralization process.

The method of deriving the required stability constants from the experimental data, in systems with step-wise equilibria, is not altogether straightforward, but the analysis of systems with successive equilibria, and the method of evaluating the measurements, have been worked out by J. Bjerrum¹⁴⁴ and others, and have been applied by Calvin,¹⁴⁵ Mellor¹⁴⁶ and others in a study of the constitutive factors, depending on the particular metal and the structure of the complexing agent respectively, which govern the formation of complex compounds.

A second quantitative approach to the problem has been based on the shift of oxidation reduction potentials accompanying complex formation, to which attention was drawn in the preceding section. In the reduction of a complex ion at a dropping mercury cathode (*i.e.* polarographic reduction), the oxidation-reduction potentials of successive stages in the process may be identified.¹⁴⁷ Thus Calvin and Bailes¹⁴⁸ found, in the reduction of a number of inner-complex salts of copper, that two 'waves' are observable, corresponding to the stages $Cu^{2+} \rightarrow Cu^+$, $Cu^+ \rightarrow Cu^0$ (amalgam) respectively. The first wave occurred at a potential which depended on the nature of the complex salt, being shifted to some more negative potential, as compared with the $Cu^{2+}-Cu^+$ potential in a simple copper solution, and being, in some cases, irreversible. The second wave, however, was truly reversible, and occurred at the same potential as in a simple copper solution. Calvin and Bailes concluded that this implied that the same entity, a simple (solvated) Cu^+ ion, was being reduced in each case at the second stage. Hence the first wave represented the disruption of the complex, as well as the transfer of one electron to the cupric ion. These two processes may be formally separated. Thus for a copper complex $[Cu X_2]$ (*e.g.* the $[Cu \text{ sal-en}_2]$ complex, (I) above), studied in a non-aqueous solvent (pyridine) because of its sparing solubility in water, the cathode reactions may be represented by three equations:



¹⁴⁴ 'Metal Ammine Formation in Aqueous Solutions', Copenhagen, 1941;
J. Bjerrum and R. Anderson, *Kgl. Danske Vidensk. Selskab.*, 1945, 22, 1.
¹⁴⁵ *E.g.* M. Calvin and K. W. Wilson, *J.A.C.S.*, 1945, 67, 2003.
¹⁴⁶ D. P. Mellor and D. E. Maley, *Austral. J. Sci. Res.*, 1949, A, 2, 92.
¹⁴⁷ For example, cf. I. M. Kolthoff and J. J. Lingane, *Polarography*, Interscience Publishers, New York, 1941. ¹⁴⁸ *J.A.C.S.*, 1946, 68, 949.

Stage Aii would take place at the half-wave potential found also for simple copper(ii) salts (+ 0.05 volts in the 50 per cent aqueous pyridine solutions used). The observed shift of the first wave then measures, directly and quantitatively, the free energy change associated with reaction Ai. This shift may, in the case of the more stable complexes, be so great that the reduction proceeds irreversibly, by a 2-electron transference, stage B occurring actually more readily than its precursor, $\text{Cu}^{2+} \rightarrow \text{Cu}^+$.

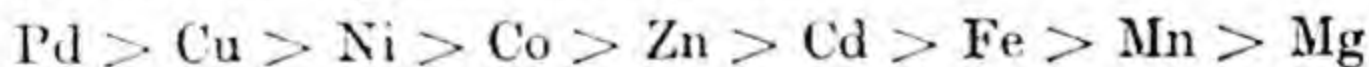
The results which have been obtained show very clearly that the structure of the chelating group affects the stability of the inner complex salt in several ways: by modifying the electron donor properties of the parent acid HX, by modifying the resonance in the double bond systems of chelating groups, and—most profoundly—by creation of rigid structures with appropriate stereochemical properties. These points are illustrated by comparison of the half-wave potentials of the examples given below.

Very similar results have been obtained with cobalt ammines; ¹⁴⁹ the first stage in reduction, $\text{Co}^{\text{iii}} \rightarrow \text{Co}^{\text{ii}}$, was again dependent on the constitution of the ammine, and affords a comparison of the stability of the different co-ordinated complexes (Table 5):

Table 5

$[\text{Co}(\text{NH}_3)_6]^{3+}$	E_2 (first stage) — 0.437 volt
$[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]^{2+}$	— 0.264 „
$[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]^+$	trans — 0.207 „
	cis — 0.043 „
$[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$	— 0.026 „
$[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]^-$	— 0.070 „
$[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$	— 0.474 „
$[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})_3]^{3+}$	— 0.249 „

Whereas the shift in redox potential has afforded a clear measure of the influence of the structure of the co-ordinating molecule, the potentiometric titration method provides a means of comparing the stability of compounds formed by any one complexing agent with various central cations. It has emerged quite clearly ^{150, 151, 152} that to a first approximation the sequence of stability is the same, irrespective of the ligands involved:



—a sequence with which Pfeiffer's earlier and qualitative results are in harmony. If a comparison is made between bivalent ions

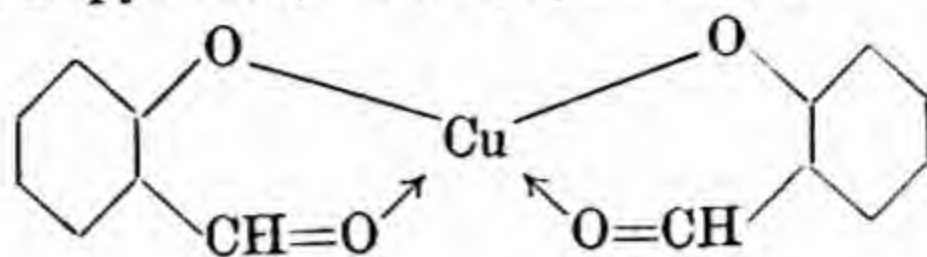
¹⁴⁹ J. B. Willis, J. A. Friend and D. P. Mellor, *J.A.C.S.*, 1945, **67**, 1680.

¹⁵⁰ D. P. Mellor and L. E. Maley, *Nature*, 1947, **159**, 370; 1948, **161**, 436, also ref. ¹⁴⁶.

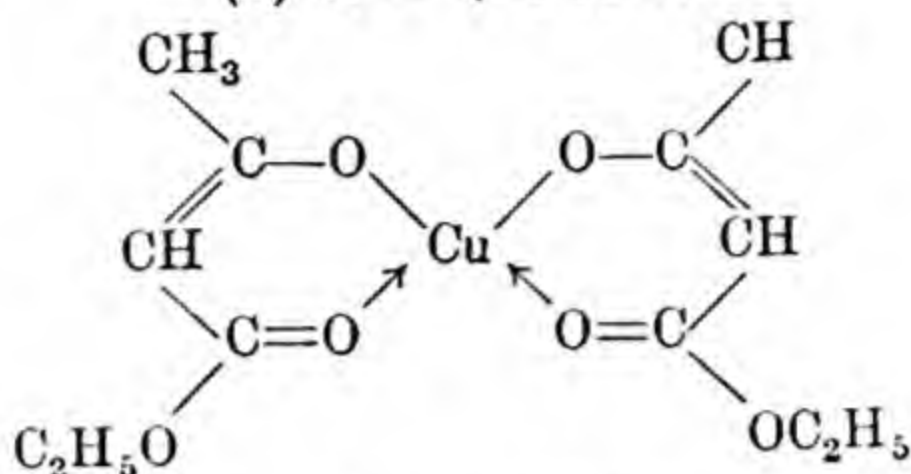
¹⁵¹ M. Calvin and N. C. Melchior, *J.A.C.S.*, 1948, **70**, 3270.

¹⁵² H. Irving and R. J. P. Williams, *Nature*, 1948, **162**, 746.

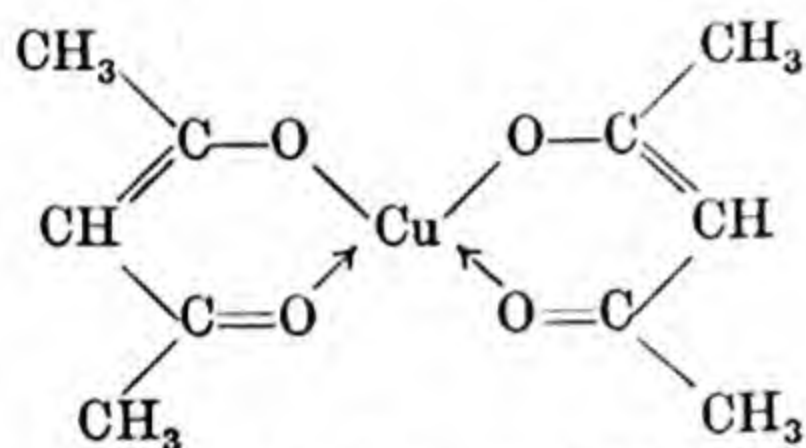
(A) Cu^{2+} (aqueous pyridine) Cu^+ (aqueous pyridine) $E = +0.05 \text{ v.}$



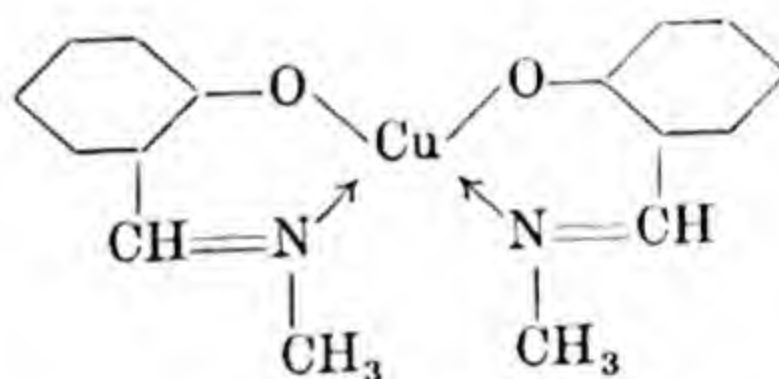
(B) $E = +0.01 \text{ v.}$



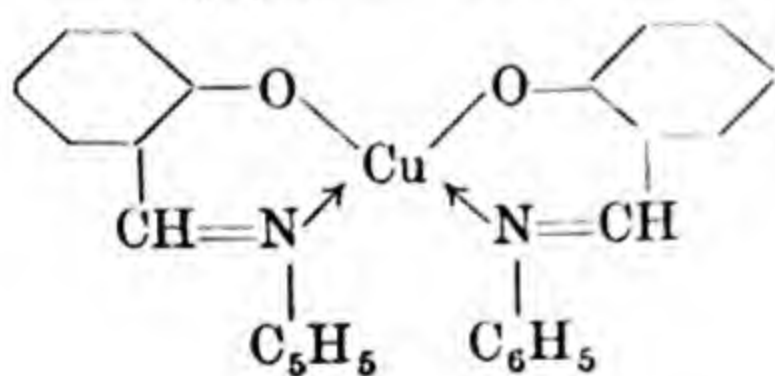
(c) $E = -0.09 \text{ v.}$



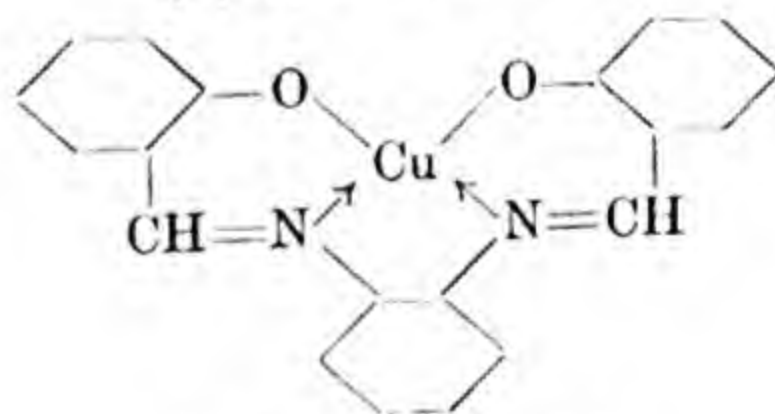
(D) $E = -0.13 \text{ v.}$



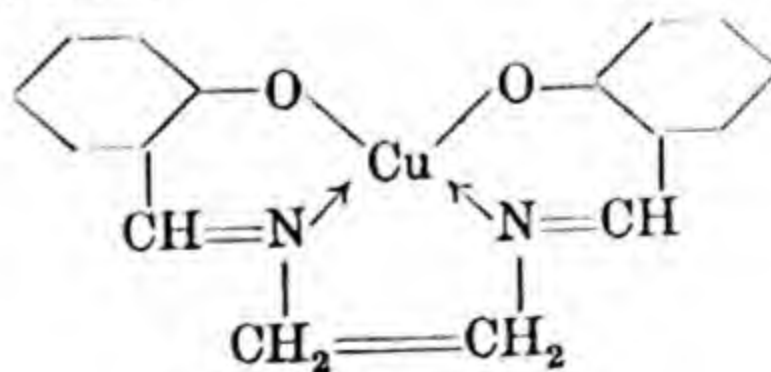
(E) $E = +0.02 \text{ v.}$



(F) $E = -0.12 \text{ v.}$



(G) $E = -0.76 \text{ v.}$



(H) $E = -0.75 \text{ v.}$

of the 1st transition series, it is evident that there is a regular trend, the maximum stability of co-ordination complexes of M^{II} being found, rather unexpectedly, with copper. Fig. 31 (due to Irving and Williams) brings this out very clearly. If ions of different

valency are compared, the sequence is changed radically, and the maximum then undoubtedly occurs with Co^{III} . The property of the central atom with which this sequence should be correlated is not yet entirely clear: it runs roughly parallel with the second stage ionization potential, and so may reflect the acceptor properties of the metal for the electrons of the co-ordinating groups.

These results bear closely upon the 'specific' function of organic reagents in analytical chemistry. Since the formation of an inner

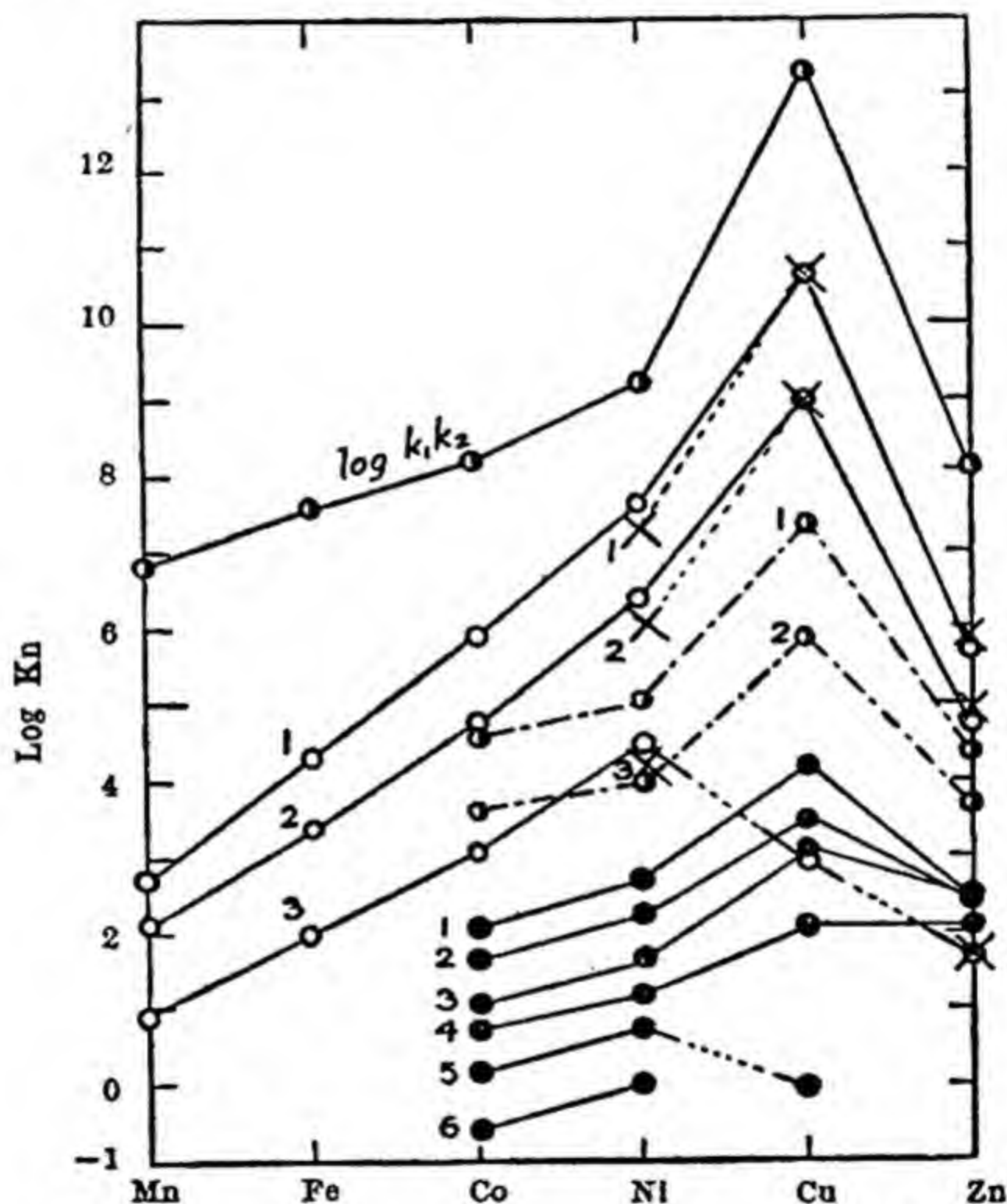
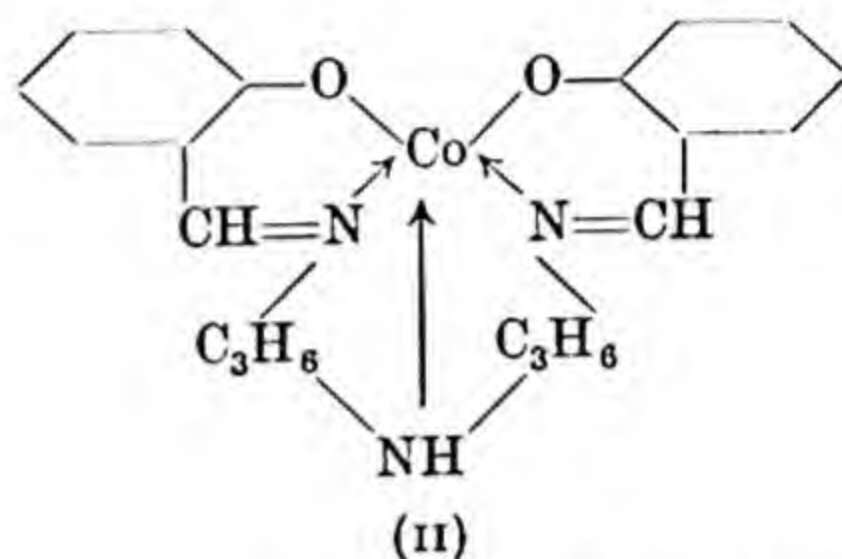
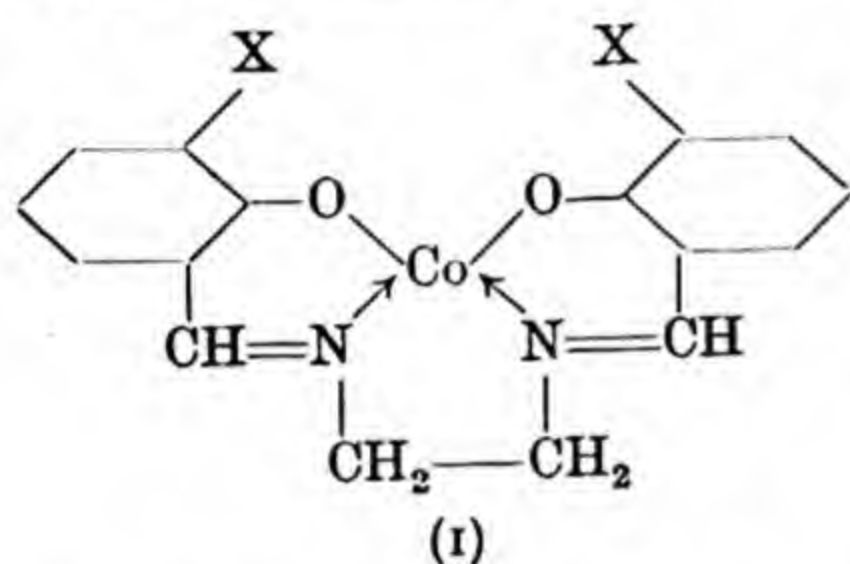


FIG. 31.—The numbers against each curve give the value of n in $\log K_n$ for: ●, ammonia; ○, ethylene diamine; ×, propylene diamine; ●, salicyl aldehyde.

complex salt involves competition of M^{n+} ions with H^+ for combination with the anions X^- , it follows that the more stable the complex, the greater is the hydrogen ion concentration at which it will persist in appreciable amounts—i.e. the higher is the hydrogen ion concentration (or the lower the $p\text{H}$ value) at which it can be precipitated or extracted by a non-aqueous solvent. Thus the minimum $p\text{H}$ at which bivalent metals of the first transition series are precipitated by oxine or by quinaldinic acid, or at which they

may be extracted by dithizone, follows a sequence agreeing exactly with the data of Fig. 31, the lowest pH of formation (*i.e.* maximum stability of the complexes) being found with Cu^{II} .

Oxygen-Carrying Complex Compounds.—Reference has been made on an earlier page to the iron-porphyrin compounds, which can combine reversibly with oxygen, and which serve as oxygen carriers in biological systems. Quite recently a synthetic series of inner complex salts—also based on a rigid quadridentate skeleton—has been discovered, with the property of absorbing molecular oxygen reversibly from the air.



Pfeiffer, in 1933,¹⁵³ observed that the red compound of cobalt with salicylaldehyde ethylenediimine (I, $X = H$) turned black in air, and Tsumaki¹⁵⁴ showed that this was due to the absorption of oxygen. In an extensive investigation, Calvin and his co-workers¹⁵⁵ have found that this behaviour is typical of the cobalt compounds of the type discovered by Pfeiffer ('salcomines'), and that the combination with oxygen (*e.g.* the dissociation pressure) is modified substantially by slight modification of the organic structures. These presumably produce inductive effects which modify the donor properties of the atoms linked to the metal.

The salcomines proper (I) are found to carry one molecule of oxygen per two atoms of cobalt; they will absorb oxygen not only in solution, but also in the solid crystalline state. For the parent salcomine (I, $X = H$) the dissociation pressure is about 50 mm. at 25° ; for the 3-fluoro compound ($X = F$), the stability of the oxygenated complex is higher, so that p_{O_2} is about 2 mm. at 25° . The compounds can undergo oxygenation and deoxygenation repeatedly, but some oxidation and decomposition occurs, so that they do not represent a useful practical means of separating oxygen from the air.

¹⁵³ *Annalen*, 1933, 503, 84.

¹⁵⁴ *Bull. Soc. Chem.*, Japan, 1938, 13, 252.

¹⁵⁵ M. Calvin, R. H. Bailes, and W. K. Wilmarth, *J.A.C.S.*, 1946, 68, 2254, 2267.

Magnetic measurements show that the compounds of type (I) have one unpaired electron, as is expected for planar covalent complexes of bivalent cobalt. The susceptibility decreases linearly with the quantity of oxygen absorbed, and is practically zero when absorption is complete—*i.e.* when $\text{Co} : \text{O}_2 = 2 : 1$. The paramagnetic oxygen molecule (*cf.* Chap. III) thus combines by sharing its two unpaired electrons with two molecules of the cobalt complex; it persists as a molecule, and is not dissociated into oxygen atoms.

Compounds derived from salicylaldehyde and propylene triamine (*e.g.* II) combine with one molecule of oxygen for each molecule of cobalt. These complexes are necessarily pyramidal in configuration. Magnetic evidence indicates essentially ionic binding, with 3 unpaired electrons; their ease of crystallization suggests the packing of molecules of a rigid framework; and the union with oxygen implies that one sector of the cage-like structure is open to reaction with the gas. The union with molecular oxygen is through the sharing of two electrons of the cobalt with the unpaired electrons of the oxygen molecule, for on complete oxygenation the magnetic susceptibility diminishes to that characteristic of a complex with one unpaired spin.

Water of Crystallization.—The formation of salt hydrates bears many analogies to the formation of ammoniates, and Werner therefore applied the co-ordination theory to the formulation of hydrates also.¹⁵⁶ A completely satisfactory classification is not possible, however, in terms of co-ordination theory alone, but the accumulation of detailed evidence concerning the structure of solids has indicated lines along which a more comprehensive classification may be developed. Under the general heading of water of crystallization several distinct functions and modes of combination are really included. Listed roughly in the sequence of decreasing tightness of binding, they may be distinguished as:

- (i) *Water of constitution*, present in the form of hydroxyl groups.
- (ii) *Co-ordinated water*, present as a neutral ligand in ammino- or acido-complexes, or filling all the co-ordination positions in aquo-cations.
- (iii) *Anion water*, pertaining to the solid state only, and associated with the anion, to which it is linked by hydroxyl bonds.
- (iv) *Lattice water*, *i.e.* water molecules occupying definite positions in the crystal structure, but not forming aquo-cations or functioning as anion water in the narrower sense. In the heavily

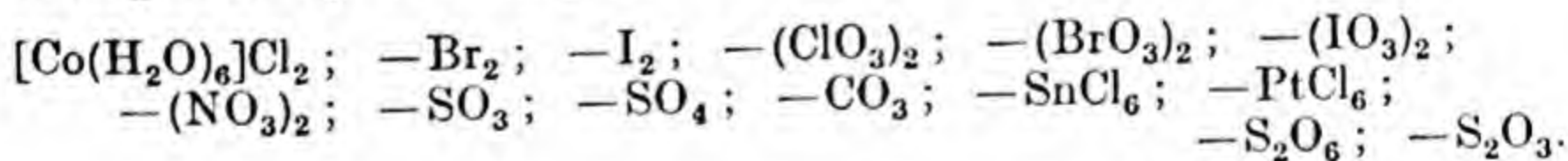
¹⁵⁶ *Cf.* Werner, *New Ideas in Inorganic Chemistry*, 1913. Weinland, *Komplexverbindungen*, 1924, p. 18 *et seq.*

hydrated salts of some oxy-acids—*e.g.* $\text{Na}_2\text{SO}_4 \cdot 12\text{H}_2\text{O}$ —and in the heteropoly acids (Chapter VII), structures are built up in which cavities are filled with water molecules. These are bonded to each other, and to the oxygen atoms of the anions, by hydrogen or hydroxyl bonds, and frequently have the same spatial arrangement as do the water molecules in ice.

- (v) *Zeolitic water.* In some heavily hydrated compounds, dehydration gives rise to a bivariant system, instead of, as ordinarily, to a univariant system with two solid phases (hydrate and dehydration product). Such water may or may not be randomly located in the crystal lattice.

Water of constitution. The role of water in the oxy-acids of the amphoteric and heavy elements will be discussed later. The hydrous oxides of the bivalent and trivalent metals are true hydroxides, as represented, for example, by the important types $\text{M}^{\text{II}}(\text{OH})_2$ ($\text{M} = \text{Ni}, \text{Mg}, \text{Fe}, \text{Zn}$ and other divalent cations) and $\text{M}^{\text{III}}\text{O} \cdot \text{OH}$ (*e.g.* $\text{FeO} \cdot \text{OH}, \text{AlO} \cdot \text{OH}, \text{MnO} \cdot \text{OH}$, etc.). These are mostly structures of layer lattice type, consisting of sheets of hydroxyl ions (or oxide and hydroxyl ions), between which are located the cations. Part of the water present in basic salts is combined in the same way. The relation of these structures to the co-ordination compounds is examined in a later section.

Co-ordinated water. Aquo-cations. The frequent occurrence of certain definite amounts of water of crystallization (*e.g.* 4 or 6 molecules per atom of metal) at once suggests its association with a complex cation. Thus the bivalent metals form a very large number of salts containing *metal : water* = 1 : 6, in which we may infer the presence of a common type of cation $[\text{M}(\text{H}_2\text{O})_6]^{2+}$. This may be exemplified by the long list of cobalt salts of this type:



Similar aquo-cations are formed by Ni, Zn, Cd, Fe, Mg, Ca, Sr, and amongst the trivalent metals by Al, Cr, Fe, Mn, Tl and others. Similarly, tetraquo-cations, $[\text{M}(\text{H}_2\text{O})_4]$, are found in salts of copper—*e.g.* $[\text{Cu}(\text{H}_2\text{O})_4]\text{SO}_4 + \text{H}_2\text{O}$; $-(\text{ClO}_3)_2$; $-\text{Br}_2$; $-\text{SiF}_6$; of beryllium— $[\text{Be}(\text{H}_2\text{O})_4]\text{SO}_4$; $-(\text{ClO}_4)_2$; and in other cases, including salts of Cr^{II} , Mn, Fe^{II} , Co and Ni.

While the formation of aquo-cations by the heavy metals is in keeping with their small ionic radii and high complex-forming power, there is some indication that the alkali metal ions also combine with water. Thus the compounds $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$, $\text{Na}_3\text{AsO}_4 \cdot 12\text{H}_2\text{O}$,

$\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$, $\text{Na}_3\text{Cr}(\text{CNS})_6 \cdot 12\text{H}_2\text{O}$, $\text{NaNH}_4\text{HPO}_4 \cdot 4\text{H}_2\text{O}$, etc., suggest the existence of the $[\text{Na}(\text{H}_2\text{O})_4]^+$ cation.

The existence of an octohedral grouping of water molecules around the metal atom in those compounds adjudged to contain $[\text{M}(\text{H}_2\text{O})_6]$ cations has been confirmed by X-ray crystallography. There is a considerable bulk of evidence that the same cations are hydrated in solution also, and certain methods of measuring ionic weights—*e.g.* the method of electrodialysis—give results which indicate the persistence in many cases of 6-co-ordinate or 4-co-ordinate hydrates. As is well known, however, the various methods of determining the hydration of ions in solution give highly discordant results.

In general, the aquo-cations correspond with the reversibly dissociable metal ammoniates, such as $\text{CoCl}_2 \cdot 6\text{NH}_3$, rather than with the amines proper, such as $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$, since they exhibit a definite dissociation pressure of water vapour, and dehydrate along discontinuous isothermal or isobaric curves. Only in the case of a few compounds, such as the chromic chloride hydrates, is the strength of binding of the water comparable with that of ammonia in the amines, so that clear-cut ionization isomerism occurs. Thus there are three isomers of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$. The violet-grey hexahydrate is shown by its equivalent conductivity in solution, by the reactivity of all its chlorine, and by the way in which it (and the salts derived from it) behave on dehydration—to be a hexaquo-chromic salt, $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$. The same cation is present in other violet chromic salts and their solutions. The dark green chromic chloride isolated from hot solutions is a dichlorotetraquo salt, $[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{Cl} \cdot 2\text{H}_2\text{O}$. Similar diacido-tetraquo cations are present in the green solutions obtained by heating other chromic salts. A third chloride, with two-thirds of its chlorine so combined as to be immediately precipitated by silver nitrate, $[\text{CrCl}(\text{H}_2\text{O})_5]\text{Cl}_2 \cdot \text{H}_2\text{O}$, was first isolated by Bjerrum in 1906.

It has also been found¹⁵⁷ that the rubidium alums of cobalt and rhodium, $\text{Rb}[\text{Co}(\text{H}_2\text{O})_6](\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Rb}[\text{Rh}(\text{H}_2\text{O})_6](\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, are both diamagnetic, as probably is hydrated cobaltic sulphate, $\text{Co}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, also. The free Co^{3+} cation would presumably have four unpaired electrons, and would certainly be paramagnetic. In these compounds, therefore, the water is evidently bound by the same kind of covalencies as are operative in the cobaltammines proper.

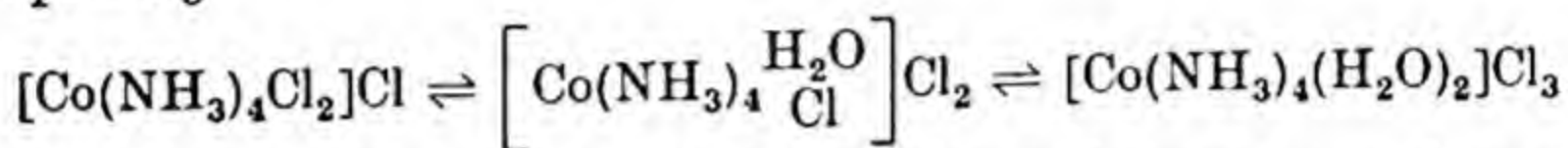
In agreement with this view, it has been found by Hunt and Traube¹⁵⁸ that in solutions of chromic salts the Cr^{3+} cation binds

¹⁵⁷ H. Bommer, *Z. anorg. Chem.*, 1941, **246**, 275.

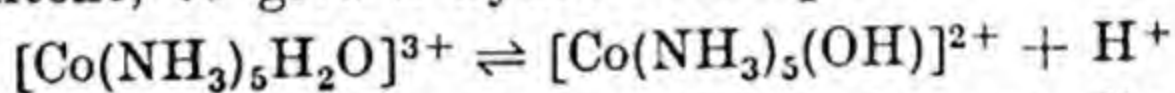
¹⁵⁸ *J. Chem. Phys.*, 1950, **18**, 757.

six molecules of water in such a way that they are exchanged only very slowly for other, free water molecules of the solvent (labelled by enrichment of H_2^{18}O); the time of half change is about 40 hours. The presence of a well-defined $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ complex, with a very small dissociation constant, is thereby established. On the other hand, the Co^{2+} cation very rapidly shares the water molecules of its hydration sheath with others from the body of the solution.

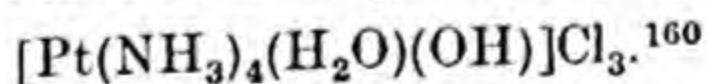
More usually, water is but loosely bound in the co-ordination complex. Considering first the aquo-ammines, in which water is but one ligand in a stable complex, it is characteristic that it is reversibly and fairly readily replaced within the complex by anionic groups—*e.g.*



Moreover, there is evidence that co-ordinated water can dissociate to some extent, to give a hydroxo-complex:



Solutions of aquopentammine cobaltic salts are distinctly acid, and the addition of alkalis immediately yields the hydroxo salts, which are alkaline in reaction. In the compounds of the heavier platinum metals, the acid function of the complex is augmented; thus, the hydroxo salt $[\text{Ru}(\text{NO})(\text{NH}_3)_4\text{OH}]\text{Br}_2$, obtained by the action of ammonia and potassium bromide upon $\text{K}_2[\text{Ru}(\text{NO})\text{Cl}_5]$, is neutral in reaction,¹⁵⁹ while the corresponding aquo salts, $[\text{Ru}(\text{NO})(\text{NH}_3)_4\text{H}_2\text{O}]\text{X}_3$, are formed only with strong acids, and readily revert to the hydroxo salts. Similarly, from the platonic dihydroxotetrammine complex $[\text{Pt}(\text{NH}_3)_4(\text{OH})_2]\text{SO}_4$, only hydrochloric acid is capable of forming an aquohydroxo salt,

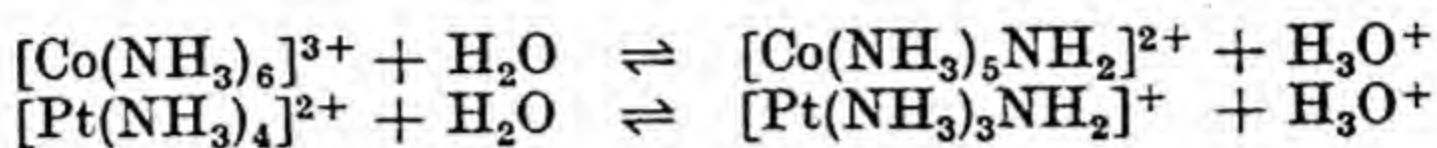


It is plain that compounds containing co-ordinated water are essentially acids in the sense defined by Brönsted. There is, however, no difference in principle between the function of water and of ammonia within the co-ordination complex. The 'acid strength' of co-ordinated ammonia is, however, much less than that of water. Thus, in the platonic ammines, hydroxo salts are readily formed, the compound $[\text{Pt}(\text{NH}_3)_4(\text{OH})_2]\text{Cl}_2$ being actually more stable than the aquo-hydroxo salt $[\text{Pt}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{OH})]\text{Cl}_3$. Amido-ammines of platonic platinum can also exist—*e.g.* the salt $[\text{Pt}(\text{NH}_3)_4(\text{NH}_2)\text{Cl}]\text{Cl}_2$, which is formed directly by the action of OH' ions on

¹⁵⁹ Werner, *Ber.*, 1907, 40, 2614.

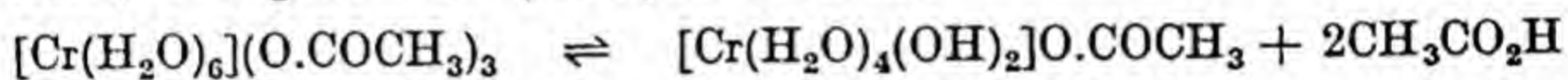
¹⁶⁰ Carlgreen and Cleve, *Z. anorg. Chem.*, 1892, 1, 65; Werner, *Ber.*, 1907, 40, 4093.

$[\text{Pt}(\text{NH}_3)_5\text{Cl}]\text{Cl}_3$.¹⁶¹ The cation $[\text{Pt}(\text{NH}_3)_6]^{4+}$ is a Brönsted acid comparable in strength with the aquopentammine cobaltic ion, and a 0.001*N* solution of $[\text{Pt}(\text{NH}_3)_6]\text{Cl}_4$ has a *pH* of 5.9.¹⁶² Although no amido complexes are known in the case of cobalt or platinous platinum, it has nevertheless been shown, from studies of the exchange of hydrogen isotopes between water and the amines of cobalt, iridium, platinum(ii) and palladium, that reactions of the type

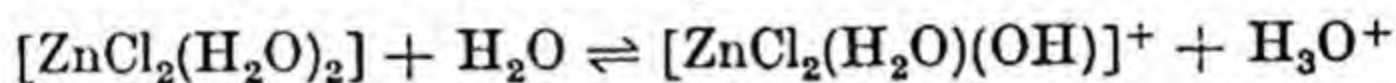


are perfectly general in occurrence.¹⁶³

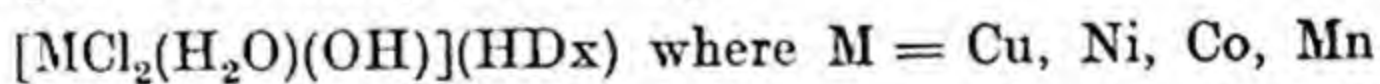
The close analogy between the aquo-complex proper and the behaviour of water (and ammonia) in amines is shown by the formation¹⁶⁴ of $[\text{Cr}(\text{H}_2\text{O})_4(\text{OH})_2]_2\text{SO}_4$. This salt is formed by the action of pyridine on chrome alum, or by the addition of sodium sulphate to chromic acetate, which is already green in dilute solutions, owing to the hydrolysis reaction



To a less marked extent, this sort of acid dissociation is a general property of salt hydrates in solution. Reiff¹⁶⁵ has shown that the acidity of aqueous solutions of metal halides can be interpreted in terms of their dissociation as aquo-acids—*e.g.*



Although metallic salts of such acids cannot generally be isolated, crystalline oxonium salts formed with cineole or dioxane (Dx) have been prepared in many cases, *e.g.*



A mechanism is thus furnished for typical hydrolytic reactions, and especially for the hydrolysis of the salts of the metals of high valency and high ionic potential. The cation in solution is surrounded by a sheath of water molecules. When, as with Zr^{4+} , the polarizing power of the cation is great enough, the dissolved aquo-complex may be a strong acid. Equilibrium then favours the

¹⁶¹ Tschugaev, *Z. anorg. Chem.*, 1924, **137**, 1, 401; *Compt. rend.*, 1915, **160**, 840; **161**, 699; A. Grünberg, *Z. anorg. Chem.*, 1924, **138**, 333; 1930, **193**, 193.

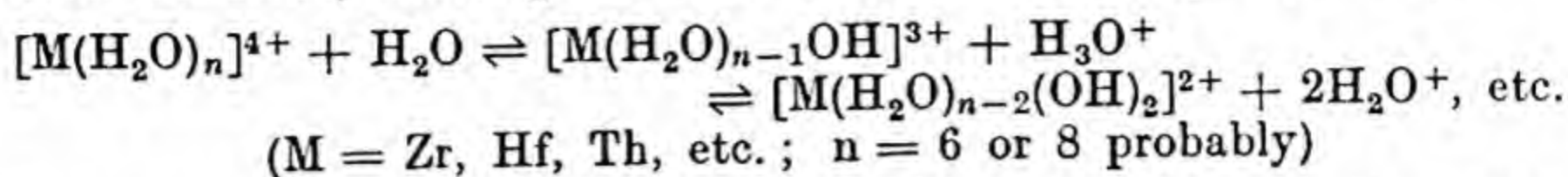
¹⁶² Cf. Grünberg and Faermann, *Z. anorg. Chem.*, 1930, **193**, 223 *et seq.*, *Acad. Sci. U.R.S.S., Mendeléef Jubilee*, 1936, 479.

¹⁶³ Anderson, Spoor and Briscoe, *J.C.S.*, 1943, 361; Anderson, Spoor, Briscoe and Cobb, *ibid.*, 367.

¹⁶⁴ Werner, *Ber.*, 1908, **41**, 3451.

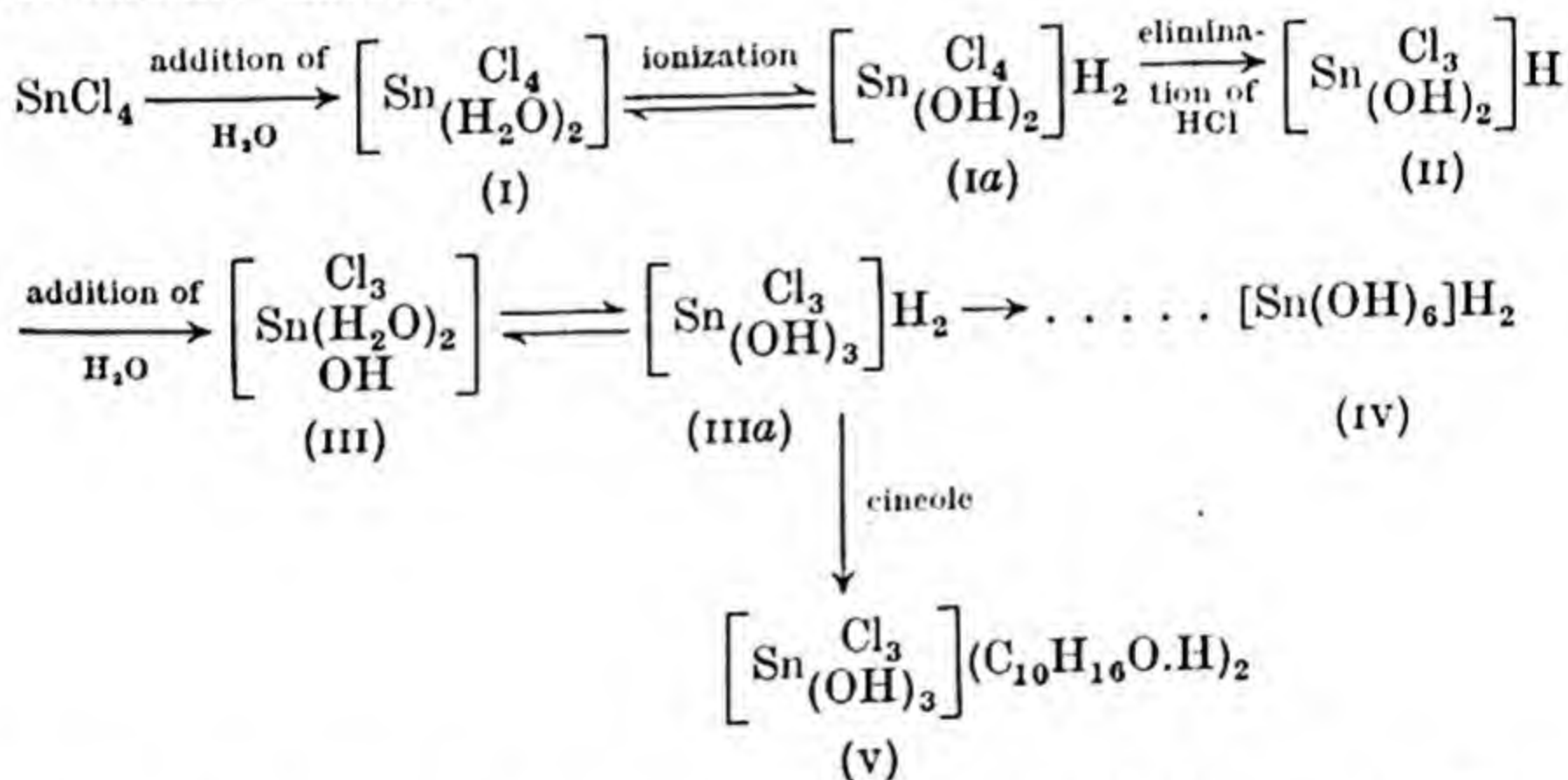
¹⁶⁵ *Z. anorg. Chem.*, 1932, **208**, 321.

hydroxo-form (the Brönsted base), with its strong electrostatic (or even covalent) binding between metal and OH' group. *E.g.*

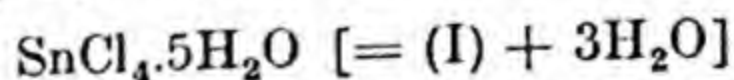


Subsequent processes, which are considered in a later section, may lead to the condensation and aggregation of the basic cations.

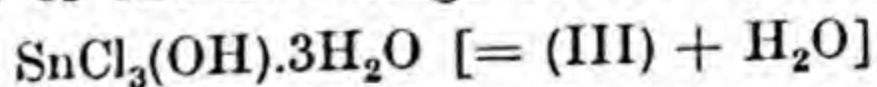
Where, as with the covalent halides of non-metallic type, no aquo-cations exist, an essential first step in the hydrolysis is the co-ordinative addition of water. This stage is followed by the intramolecular elimination of halogen acid, and in this second stage the acid dissociation of the co-ordinated water is the essential operative mechanism. This may be illustrated by the hydrolysis of stannic chloride :



Since the immediate product of elimination of halogen acid (II) is co-ordinatively unsaturated, water is again co-ordinated, and the process continues until hydrolysis is complete (IV). In the case of stannic chloride, the initial addition compound



and the product of the first stage of the hydrolysis,

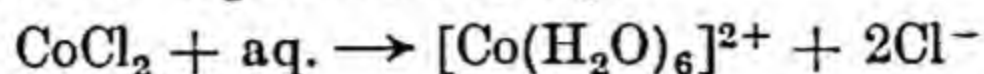


are both known. The acid nature of the latter compound, as required by the above mechanism, is shown by the formation of a salt (V) with cineole.¹⁶⁶

Such a mechanism for the hydrolysis of the covalent halides at once makes clear the fundamental differences between these and the

¹⁶⁶ Pfeiffer and Angern, *Z. anorg. Chem.*, 1929, 183, 189.

electrovalent halogen salts—the metallic halides proper. Dissolution of the latter compounds in water leads, in the typical case, to the formation of an aquo-cation, *e.g.*—



The special position of sulphur hexafluoride and carbon tetrachloride amongst the non-metallic halides is also comprehensible, since in these compounds the co-ordination maximum of the central atom is already attained. The necessary initial additive step therefore does not take place. Tungsten hexachloride is again hydrolysable, however, since the co-ordination maximum for tungsten is 8 (as in $\text{K}_4[\text{W}(\text{CN})_8]$). Stability to hydrolysis may be expected when the co-ordinative addition of water is once more excluded by the attainment of the co-ordination maximum in OsF_8 .

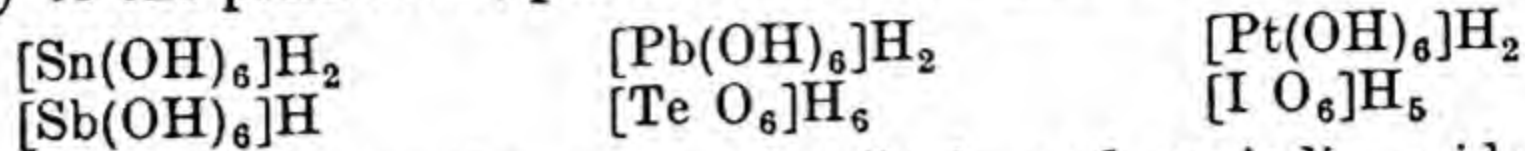
Oxy-acids.—The views just developed provide a very general approach to the theory of the oxy-acids of the elements. These may be subdivided roughly into three classes:

- (a) *Simple oxy-acids*, formed by the lighter, strongly electronegative elements. The composition of these oxy-acids is governed primarily by direct considerations of the valency of the central atom, and there is little tendency to form true ortho-acids.
- (b) *Complex oxy-acids*, formed by the heavier, weakly electronegative or amphoteric elements, such as tellurium, iodine and antimony. The composition of these is determined by the necessity of completing the co-ordination sphere of the central atom. To this group belong the salts formed by amphoteric metallic hydroxides.
- (c) *Poly-acids*, formed by the elements of groups VA and VIA—*viz.* V, Nb, Ta, Mo, W and U. These acids, discussed in detail in a later chapter, represent co-ordination structures of a very special type.

The second group, here termed complex oxy-acids, are of importance in that they were early recognized as establishing a connexion between the chemistry of the co-ordinated complex and that of compound formation by means of primary valencies. The oxy-acids of Sn^{IV} , Pb^{IV} , Pt^{IV} , Sb^{V} , Te^{VI} , and I^{VII} fall within this group. Thus, the alkali plumbates and stannates all contain three molecules of water—*e.g.* $\text{Na}_2\text{O}.\text{SnO}_2.3\text{H}_2\text{O}$ —which is lost only at temperatures considerably above 100° , when complete decomposition of the salts takes place simultaneously.¹⁶⁷ No salts have been prepared with less than $3\text{H}_2\text{O}$; those salts with more water—*e.g.* $\text{BaO}.\text{SnO}_2.7\text{H}_2\text{O}$

¹⁶⁷ Belucci and Parravano, *Z. anorg. Chem.*, 1905, **45**, 142.

—lose water readily down to that amount. The salts may therefore be derived from an anion $[\text{Sn}(\text{OH})_6]^{2-}$, in which the 6-co-ordination shell of the tin is filled; the removal of the constitutional water breaks up the complex anion completely. Similar considerations apply to the plumbates, platينات, etc., which are salts of the acids



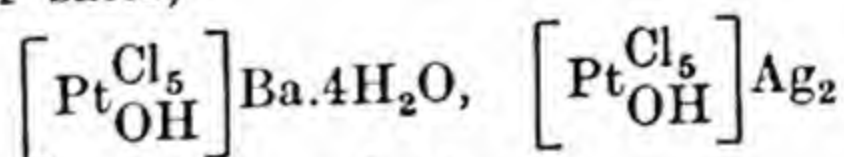
As is plain from the cases of telluric and periodic acids, the basicity of the acids is variable. The composition of the salts varies especially with the size (ionic radius) of the cation concerned. The maximum basicity is frequently displayed in the silver salts, as in Ag_6TeO_6 and Ag_5IO_6 ; the bulky alkali ions more commonly form acid salts, as, for example, $\text{K}_2[\text{Te}(\text{OH})_4\text{O}_2]$ and $\text{Na}_3[\text{I}(\text{OH})_2\text{O}_4]$.

Although the 6-co-ordinated form is the normal for these acids, the existence of other forms is not excluded, as is shown, for example, by the existence of metaperiodic acid HIO_4 , and mesoperiodic acid $\text{H}_4\text{I}_2\text{O}_9$.

The close relationship between the oxy-acids and those compounds usually regarded as co-ordination compounds is particularly emphasized by the nearly complete series of transition between $\text{H}_2[\text{PtCl}_6]$ and $\text{H}_2[\text{Pt}(\text{OH})_6]$, worked out by Miolati¹⁶⁸ and outlined below:

(a) By heating hydrated chlorplatonic acid, $\text{H}_2[\text{PtCl}_6].6\text{H}_2\text{O}$, at 98° under 100 mm. pressure, one molecule of hydrochloric acid is lost, and a compound $\text{PtCl}_4.\text{HCl}.\text{H}_2\text{O}$ remains, which is soluble in water, the solution having about the same equivalent conductivity ($\Lambda = 393$) as oxalic acid. It behaves as a dibasic acid, and must

be ascribed the formula $[\text{Pt}(\text{Cl}_5\text{OH})]\text{H}_2$, in accordance with which barium and silver salts,



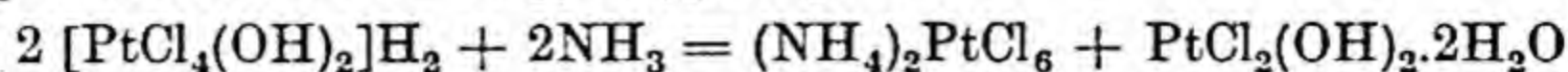
may be obtained from the solution.

(b) The hydrate of platonic chloride, $\text{PtCl}_4.5\text{H}_2\text{O}$, itself forms a strongly acid aqueous solution, requiring two equivalents of sodium hydroxide for neutralization. It thus reacts as the dihydroxo-acid

$[\text{Pt}(\text{Cl}_4(\text{OH})_2)]\text{H}_2.3\text{H}_2\text{O}$, and as such forms the yellow silver salt $[\text{Pt}(\text{Cl}_4(\text{OH})_2)]\text{Ag}_2$ on addition of silver nitrate.

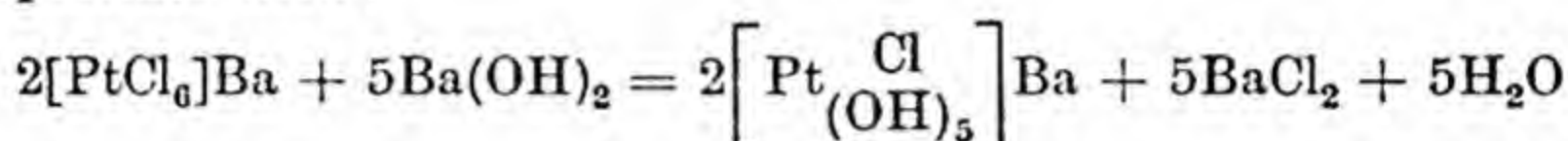
¹⁶⁸ *Z. anorg. Chem.*, 1900, 22, 445; 1901, 26, 209; 1903, 33, 251.

(c) With a small amount of ammonia, this dihydroxo-acid reacts to form ammonium chlorplatinate and a new compound with the empirical formula $\text{PtCl}_2(\text{OH})_2 \cdot 2\text{H}_2\text{O}$:



This compound, since its aqueous solution reacts acid, is to be regarded as tetrahydroxo-acid $\left[\text{Pt} \begin{smallmatrix} \text{Cl}_2 \\ (\text{OH})_4 \end{smallmatrix} \right] \text{H}_2$, and gives silver, lead, and mercury salts, $\left[\text{Pt} \begin{smallmatrix} \text{Cl}_2 \\ (\text{OH})_4 \end{smallmatrix} \right] (\text{Ag}_2, \text{Pb}, \text{Hg})$.

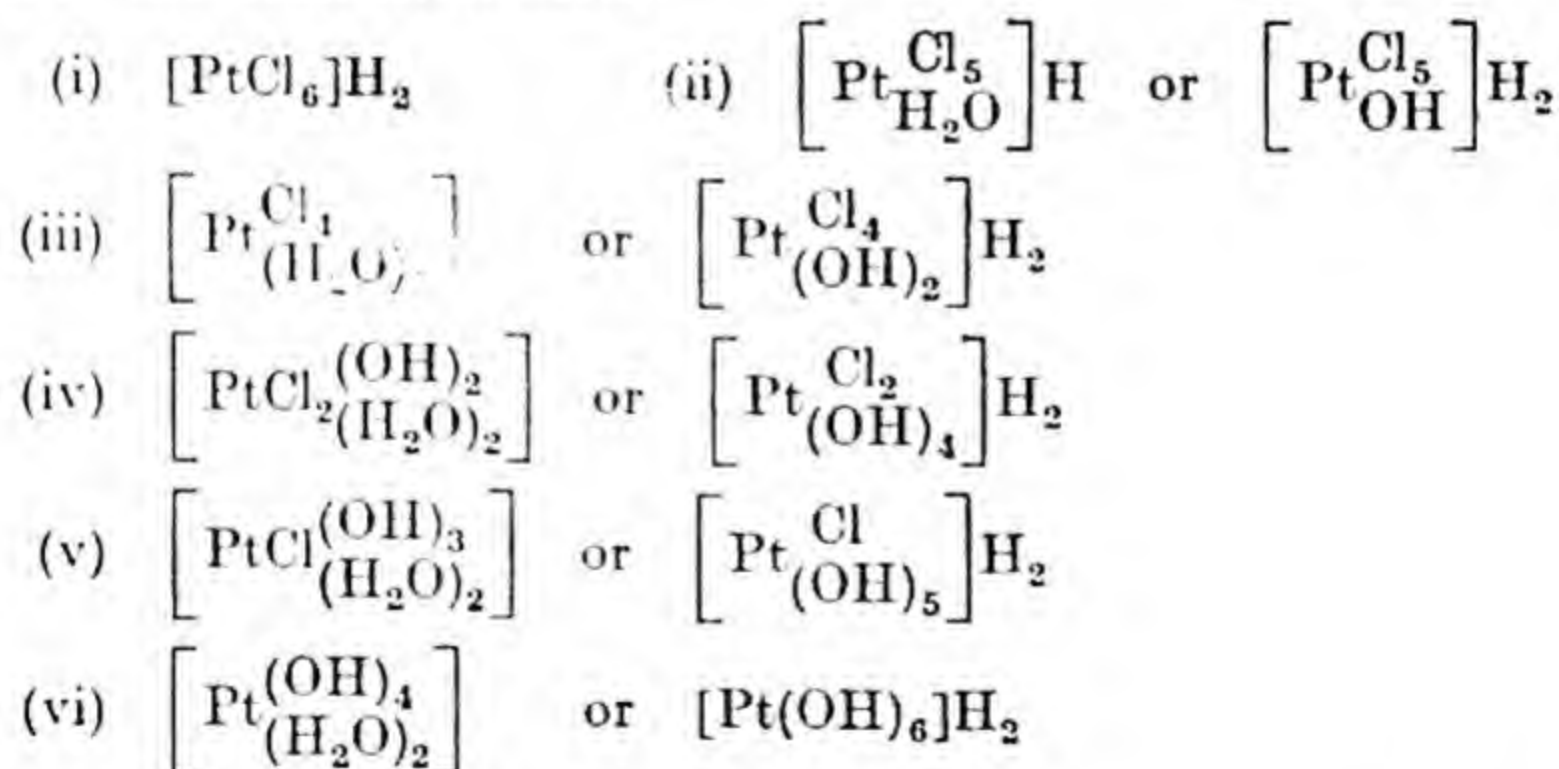
(d) The alkaline earth hydroxides react in sunlight with the corresponding chlorplatينات, forming the salts of a pentahydroxo-chlorplatinate acid :



From the alkaline earth salts, the salts of heavy metals may be prepared.

(e) The final stage of the progressive substitution is reached in platinate acid itself, the well-crystallized alkali salts of which are obtained by the action of caustic alkalis upon sodium chlorplatinate. These contain three molecules of constitutional water—*e.g.* $\text{K}_2\text{O} \cdot \text{PtO}_2 \cdot 3\text{H}_2\text{O}$ —and from them, by the action of acetic acid, hydrated platinate oxide, $\text{PtO}_2 \cdot 4\text{H}_2\text{O}$, is obtained. They thus agree in composition with the requirements of the co-ordination formula $[\text{Pt}(\text{OH})_6]\text{R}_2$.

Thus the transition series



is known in its entirety.

The theory of the oxy-acids developed in this section applies also to the formation of salts by the hydroxides of the amphoteric metals. The solubility of the hydroxides of the transition metals in caustic alkali has long been known. The isolation, in a pure state, of the

salts so formed is a matter of some experimental difficulty, and the view has at times been expressed that the phenomenon was one of colloidal peptization rather than of true salt formation. However, Scholder and Hendrich¹⁶⁹ were able to prove the existence of the hydroxo-zincates by a detailed phase rule study, and with his co-workers Scholder¹⁷⁰ has obtained, in pure crystalline form, the hydroxo-zincates, -cadmates, -plumbites, -stannites, -cobaltites, -cuprites, -chromites and -ferrites. In every case the compounds retain as much tenaciously bound (constitutional) water as corresponds to their formulation as hydroxo-complexes. In a number of instances, as for the hydroxoantimonate $[\text{Sb}(\text{OH})_6]^-$, hydroxoantimonite $[\text{Sb}(\text{OH})_4]^-$ and germanate $[\text{Ge}(\text{OH})_6]^{2-}$ anions, Brintzinger¹⁷¹ has determined the ionic weights, by the dialysis method. In every case the value found for the anionic weight corresponds with that required if the salt is to be formulated as a hydroxo-complex.

Thus, from alkali zincate solutions there may be isolated, according to conditions, salts of the type $[\text{Zn}(\text{OH})_3]\text{Na} \cdot 3\text{H}_2\text{O}$ and $[\text{Zn}(\text{OH})_4]\text{Na}_2 \cdot 2\text{H}_2\text{O}$. By double decomposition with barium and strontium hydroxides, salts of co-ordination number 6—e.g. $[\text{Zn}(\text{OH})_6]\text{Ba}_2$ —are formed.

Cobaltites and cuprites are of the same types, the typical compounds being $[\text{M}(\text{OH})_4]\text{Na}_2$, $[\text{M}(\text{OH})_6]\text{Ba}_2$, where $\text{M} = \text{Cu}^{\text{II}}$, Co^{II} or Fe^{II} .

Trivalent iron, chromium and bismuth, in the ferrites,¹⁷² chromites, and bismuthates, are said to attain the co-ordination number 8, forming the compounds $[\text{M}(\text{OH})_8]\text{Na}_5 \cdot 4\text{H}_2\text{O}$ and $[\text{M}(\text{OH})_7]\text{Na}_4 \cdot 2-3\text{H}_2\text{O}$, which are isomorphous, in addition to the simpler type $[\text{Cr}(\text{OH})_6]\text{Na}_3$. The case of the stannites and plumbites is one of particular interest, since Hantzsch,¹⁷³ by analogy with carbon, endeavoured to justify the formulation of these compounds

as the counterpart of the formates— $\text{H.M.} \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{O.Na.} \end{array}$ Scholder¹⁷⁴

found the only type of alkali salt to be $[\text{Sn}(\text{OH})_3]\text{Na}$, whereas with the alkaline earths both the trihydroxo-salts—e.g. $[\text{Sn}(\text{OH})_3]_2\text{Ba}$ —

¹⁶⁹ *Z. anorg. Chem.*, 1939, **241**, 76.

¹⁷⁰ *Z. anorg. Chem.*, 1933, **215**, 355; **216**, 138, 159, 176; 1934, **217**, 214; **220**, 411.

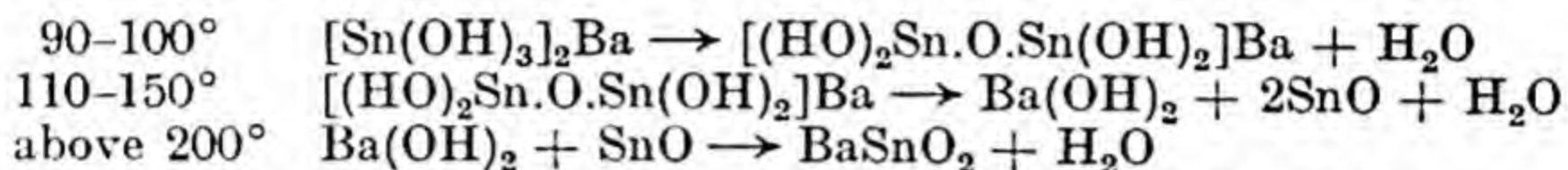
¹⁷¹ In FIAT Review of German Science 1939–45, Inorganic Chemistry, (Vol. 25), Part III, p. 8.

¹⁷² Scholder, *Angew. Chem.*, 1936, **49**, 255.

¹⁷³ *Z. anorg. Chem.*, 1902, **30**, 289.

¹⁷⁴ *Ibid.*, 1933, **216**, 176.

and, at higher temperatures an anhydro-salt of the composition $[(\text{HO})_2\text{Sn.O.Sn}(\text{OH})_2]\text{Ba}$ are formed. The relation of the hydroxo-salts formed in solution to the salts formed by fusion processes is clearly shown in the degradation of the stannites. The anhydrous barium salt $[\text{Sn}(\text{OH})_3]_2\text{Ba}$ loses half a molecule of water per atom of tin at $90\text{--}100^\circ$, undergoing conversion to the anhydro-salt. This loses a further half-molecule of water at $110\text{--}150^\circ$, corresponding to the second stage of reaction, while at temperatures above 200° the remaining half-molecule of water is lost very slowly as BaSnO_2 is formed:



The oxidation of boiling solutions of $[\text{Fe}(\text{OH})_4]\text{Na}_2$ in very concentrated (60 per cent) caustic soda yields a red sodium ferrite, NaFeO_2 , identical with that obtained by fusion of ferric oxide with sodium hydroxide. Oxidation in more dilute alkali (50 per cent), however, gives rise to an apparently isomeric green NaFeO_2 which differs from the other in that it is decomposed by dilute alkalis.¹⁷⁵

Whilst the dissolution of aluminium hydroxide in caustic alkalis undoubtedly conforms to the same general pattern, the compounds characterized hitherto appear to be complex. A variety of crystalline alkali salts has been isolated by various workers:¹⁷⁶ all contain water of constitution, but none conforms to the simple types of hydroxo-anion considered above. According to Scholder and Brintzinger, they possess high ionic weights in solution, and are probably to be regarded as condensed oxo-hydroxo salts.

Although the evidence for the constitution of the complex oxy-acids seems quite conclusive, an unexpected result has emerged from the determination of the crystal structure of typical salts—sodium stannate, $\text{Na}_2[\text{Sn}(\text{OH})_6]$, and potassium platinate, $\text{K}_2[\text{Pt}(\text{OH})_6]$.¹⁷⁷ These prove to be isomorphous with brucite, $\text{Mg}(\text{OH})_2$ —i.e. they are layer lattice structures, built up by the insertion of Sn^{4+} and Na^+ (or Pt^{4+} and K^+) ions, on more or less equal footing, into the octohedral interstices between double sheets of OH^- ions. Whilst these sheets might formally be considered as built up by packing the octohedral $[\text{M}(\text{OH})_6]^{2-}$ anions around the alkali cations, it does in fact appear that, in the solid salts, there is no essential difference in the forces operating between the OH^- groups and the two species of cations. The interpretation may,

¹⁷⁵ Scholder, *Angew. Chem.*, 1936, 49, 255.

¹⁷⁶ Cf. ref. ¹⁷¹; Fricke and Iuaitis, *Z. anorg. Chem.*, 1930, 191, 129.

¹⁷⁷ Björling, *Arkiv. Kemi Min.*, 1941, 15B, No. 2.

perhaps, be found in the weakness of the binding forces in these complex ions. In solution, the alkali cations are surrounded by a hydration sheath, and their polarizing action is minimized; the anion itself then exists as the dissociated form of an aquo-complex. The crystalline compound—as in many other instances—is not built up directly from the ionic species existing in the solution, but by the accretion of the anions and of *unhydrated* cations to the growing crystal lattice. If the complex anion is large and highly polarizable—as is the case—even the unhydrated alkali cations may have a sufficient polarizing power to impose a structure in which the separate identity of the hydroxo-anions is lost.

This relationship between very weakly bound complex ions and the crystalline compounds derived from them is not unique. Thus, whereas in Group IV of the Periodic System, Si, Ti, Zr and Hf give rise to hexafluoro-complexes, based on the complex anion $[\text{MF}_6]^{2-}$, it has been found that with the largest and least strongly polarizing quadrivalent ions K_2ThF_6 and K_2UF_6 form crystal lattices with the same structure as CaF_2 , whilst BaThF_6 and BaUF_6 are isomorphous with LaF_3 . There is thus no complex anion in the solid—these compounds can properly be written as $[\text{K}_3\text{M}_3]\text{F}_2$ and $[\text{Ba}_4\text{M}_4]\text{F}_3$ respectively. In the same way, the very weak complex $[\text{YF}_4]^-$ has no existence in the high-temperature crystalline modification of NaYF_4 , which could be written as $[\text{Na}_4\text{Y}_4]\text{F}_2$.¹⁷⁸

Basic Salts.—The well-defined basic salts of the bivalent metals—*e.g.*

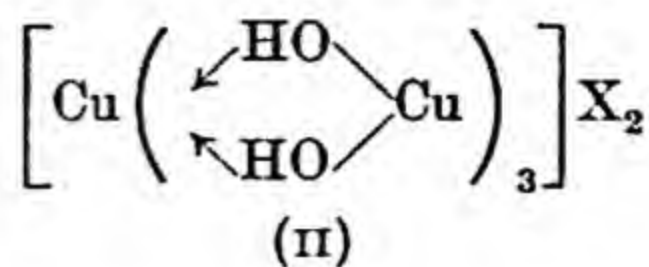
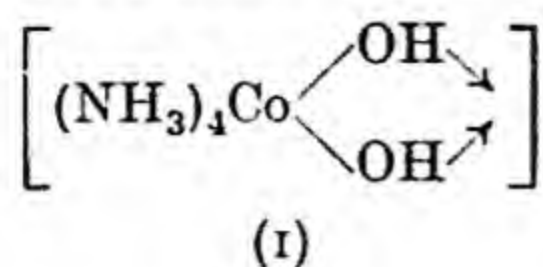
atacamite	$\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$
malachite	$\text{CuCO}_3 \cdot 3\text{Cu}(\text{OH})_2$
basic zinc nitrate	$\text{Zn}(\text{NO}_3)_2 \cdot 3\text{Zn}(\text{OH})_2$
basic cobalt carbonate	$\text{CoCO}_3 \cdot 3\text{Co}(\text{OH})_2$

all contain the normal salt and hydrous oxide in simple ratios, very often (as in the cases cited) as 1 : 3. The amount of water found analytically in all basic salts is sufficient to permit of the oxide being present in the hydrated form, as shown. Where the literature indicates exceptions to this rule it is probable that the compounds require more precise characterization.

To Werner¹⁷⁹ these facts suggested that a common structural basis for all such basic salts could be found in the Co-ordination Theory. Although his view has been superseded, it contains some suggestive elements that are still worth consideration. In brief, Werner considered that the metal hydroxide in basic salts played a role like that of the di-ol groups in polynuclear cobaltammines (I), so that the basic copper salts could all be represented as (II).

¹⁷⁸ F. Hund, *Z. anorg. Chem.*, 1950, **261**, 106.

¹⁷⁹ *Ber.*, 1907, **40**, 4441.



It is, however, to be noticed that on this hypothesis of discrete cationic complexes, only one of the metallic atoms achieves coordinative saturation. Furthermore, the reason for the extreme insolubility of the basic salts (as compared with other complex halides, sulphates, etc.) is not immediately apparent.

More recent work, and especially that of Feitknecht¹⁸⁰ on the structure of basic salts of bivalent metals, has led to a different and more precise view. This provides a further insight into the relationships between the structural principles of the free co-ordination complex and those of the crystal lattice.

The hydroxides of the bivalent metals crystallize in the hexagonal system and form layer lattices of the cadmium iodide type: that is to say that the hydroxyls form sheets of oxygen atoms, in the interstices of which the metallic atoms are so inserted as to place each between six oxygen atoms. Each sheet then represents a giant molecule of the hydroxide, and to this fact the insolubility of the hydroxides is due. The significance of one member of this group of hydroxides, brucite, $\text{Mg}(\text{OH})_2$, for the silicate and clay mineral structures is dealt with in a later chapter.

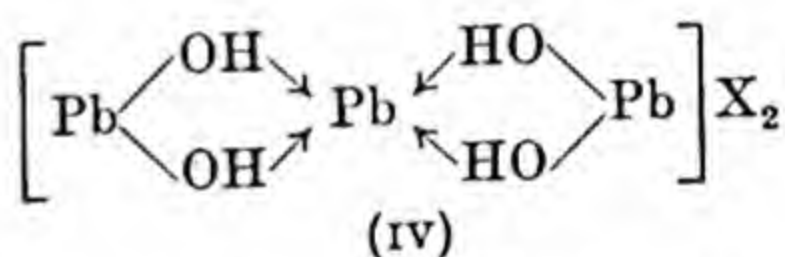
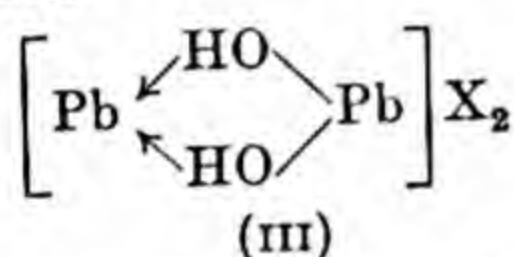
Feitknecht has found that the hydroxide structure persists, in its essentials, in the basic salts, so that in the basic zinc salts there are layers of hydroxide interleaved with layers containing the metal ions and acid anions. The spacing between the layers may be variable, and the intermediate layers may be almost unordered in structure. The possibility thus arises of the ready formation of non-stoichiometric compounds by the entry of variable proportions of metal salt into the intermediate layers. It would seem from Feitknecht's work, however, that these double layer lattice structures are metastable and tend in each case to form a compound of the formula $\text{MX}_2 \cdot 3\text{M}(\text{OH})_2$ as the limiting type. The structure of these limiting salts is based closely on the original hydroxide. As before, metal atoms are fitted into the interstices of a double layer of hydroxyl ions. If one-fourth of the hydroxyls be replaced isomorphously (see Chap. IV, p. 80) by chlorine or other univalent ions, the result is to give a slightly expanded hydroxide structure with the gross composition $\text{M}(\text{OH})_{1.5}\text{X}_{0.5}$, or $\text{MX}_2 \cdot 3\text{M}(\text{OH})_2$. It seems that this represents the characteristic structure of the basic

¹⁸⁰ *Helv. Chim. Acta*, 1933, **16**, 427, 1302; 1930, **13**, 22; 1935, **18**, 28, 40; 1936, **19**, 448, 467, 831. *Angew. Chem.*, 1939, **52**, 202.

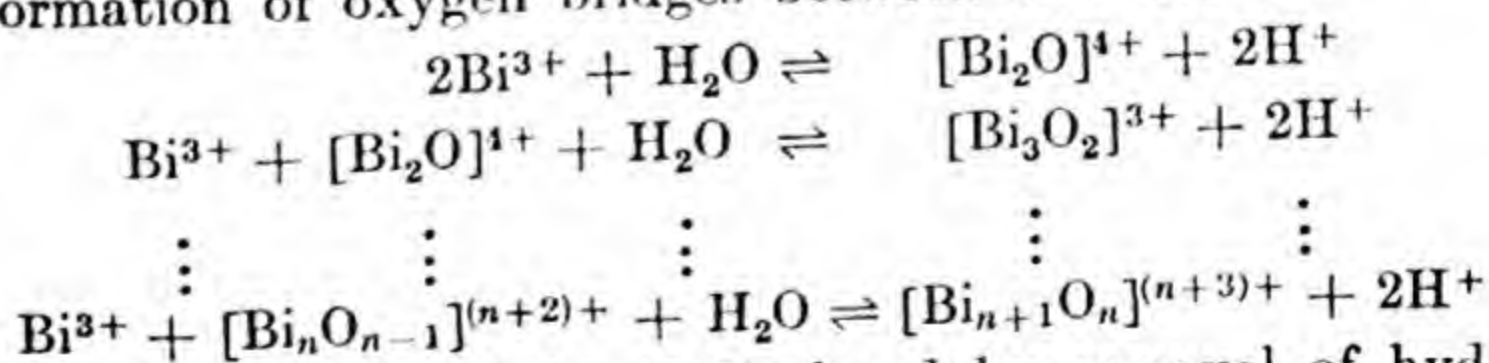
salts. As in the case of the hydroxides, each layer is a giant molecule. The existence of compounds with very variable ratios of normal salt to hydroxide, the insolubility of the basic salts, and their variable water content are thereby accounted for.

It is legitimate to see in this kind of structure a logical extension of Werner's conception, whereby all the metallic atoms, and not only one unique central atom of the complex, can attain their co-ordination maximum, by the sharing of oxygen atoms. The result is a sort of inorganic polymerization: each macro-molecular sheet of the crystal represents an 'infinitely polynuclear' complex.

Within recent years, fresh light has been cast on the processes whereby such structures may be built up from the free, isolated cations. Lead forms a well-known series of basic salts, frequently formulated as $\text{Pb}(\text{OH})\text{X}$, which would have been considered, on the Werner model, to be dimeric (III). There is also a second series, $\text{PbX}_2 \cdot 2\text{Pb}(\text{OH})_2$ (IV). In general, basic salts are notable for their extreme insolubility, but Weinland, Stroh and Paul¹⁸¹ claimed that unstable soluble perchlorates and chlorates of both series of basic lead salts could be isolated. They showed, by measurements of electrical conductivity, that in each case a bivalent cation was present



In other instances, the precipitation of a metallic hydroxide, or a basic salt, may involve as its precursors a succession of reversible, stable or metastable equilibria, which govern the processes of hydrolysis and aggregation. Granér and Sillén¹⁸² showed, for the deposition of bismuth oxy-salts from bismuth salt solutions, that the neutralization curves could be analysed to give a quantitative account of the successive reactions involved. The results accorded well with the idea that as the hydrogen ion concentration is reduced, polynuclear cations are built up by the hydrolysis reaction, through the formation of oxygen bridges between Bi^{3+} ions.



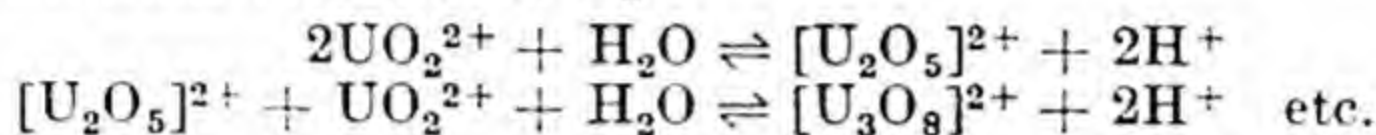
These successive equilibria, if displaced by removal of hydrogen

¹⁸¹ *Ber.*, 1922, 55, 2706; *Z. anorg. Chem.*, 1923, 129, 243.

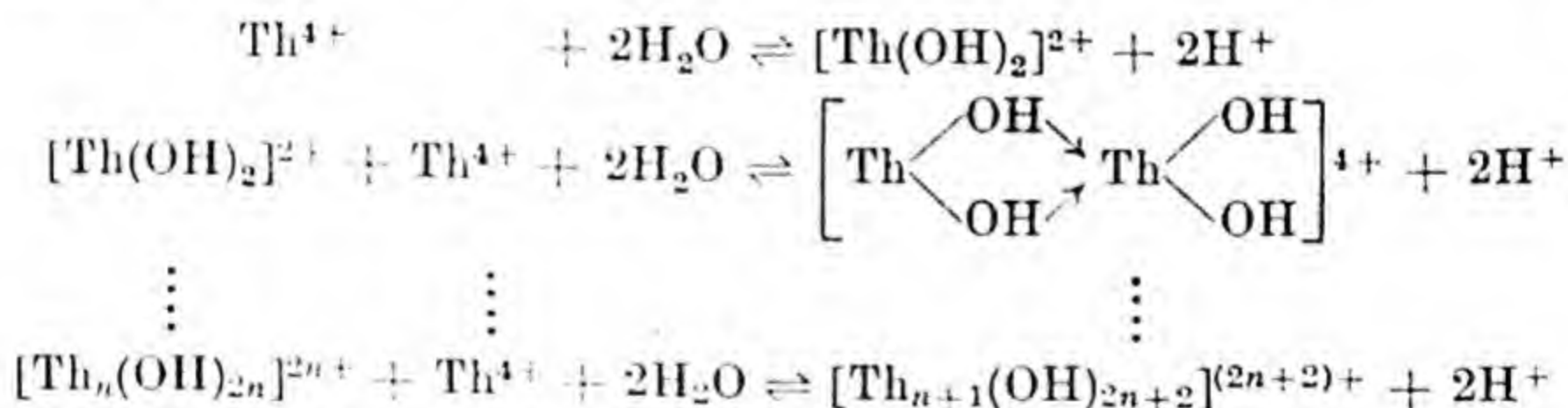
¹⁸² *Acta Chem. Scand.*, 1947, 1, 631.

ions from the solution, build up high molecular cationic complexes in the manner shown. The magnitude of the equilibrium constant at each stage determines the importance of the steps that are intermediate between the first hydrolysis product and the ultimate infinite complex, which approximates increasingly closely to the formula $[\text{BiO}^+]_\infty$. The oxygen bridging binds the atoms of the polymeric cation into a sheet structure, which occurs as an actual structural unit in a variety of basic bismuth salts¹⁸³ such as BiOCl , and the series of basic double salts investigated by Sillén.

The evidence is clear that this type of hydrolytic mechanism is fairly general. Thus, it has been shown¹⁸⁴ that in the potentiometric titration of uranyl salts with alkalis, polycationic species of successively increasing complexity are formed as the hydrogen ion concentration is reduced, *e.g.*



The mechanism of hydrolysis of the quadrivalent cations (*e.g.* Zr^{4+} , Hf^{4+} , Th^{4+}) has been but little studied, though it is familiar that their aquo-cations, $[\text{M}(\text{H}_2\text{O})_n]^{4+}$, are very strong acids. According to Lundgren and Sillén¹⁸⁵ polynuclear cations are involved in this process also. If, as with the basic bismuth salts, the hydrolysis takes place in such a way as to pre-form, in the solution, the unit which has to be built on to the growing crystal lattice as a basic salt crystallizes from the solution, the process can probably be written as—



The condensed basic cations represented in this way would be one-dimensional complexes, of the nature of linear inorganic polymers. Lundgren and Sillén base this mechanism on the observed fact that such linear cationic complexes constitute structural units in the basic thorium salt $[\text{Th}(\text{OH})_2]\text{CrO}_4 \cdot 2\text{H}_2\text{O}$.

¹⁸³ Bannister and Hey, *Mineralogical Mag.*, 1935, 24, 1949; Sillén, *Naturwiss.*, 1942, 30, 318; Lagerkrantz and Sillén, *Arkiv. Kemi*, 1948, 35A, No. 20.

¹⁸⁴ Faucherre, *Compt. rend.*, 1948, 227, 1367; Longworth, MDDC Report No. 911 (U.S.A. Atomic Energy Commission); Sutton, *J.C.S.*, 1949, S275.

¹⁸⁵ *Naturwiss.*, 1949, 36, 345.

It may be noted that the condensation processes discussed involve only simple collisions between the reacting, hydrated ions, and not—as formally written—complicated and kinetically improbable events. The essential reaction at each stage hinges on the acidic nature of the aquo-complex. Not only does a new and coherent approach to the nature of the basic salts emerge from those ideas, but there is emphasized the existence and the importance of the stages intermediate between the isolated, mononuclear Werner complex, and the infinite atomic array of the completed crystalline structure.

CHAPTER VII

POLY-ACIDS AND SILICATES

It has been pointed out in the previous chapter that oxy-acids may be classified roughly into three types :

- (a) The oxy-acids of the lighter non-metals—*e.g.* HNO_3 , H_2SO_4 . The composition of the acids is determined primarily by the valency of the central atom, and there is little tendency to form true ortho-acids or salts.
- (b) The oxy-acids derived from the weakly electronegative and amphoteric elements have their constitution determined by the co-ordination number of the central atom. Thus, corresponding to the co-ordination number six for tin, antimony, tellurium, iodine and platinum, the oxy-acids of these elements are correctly represented by the formulæ $[\text{Sn}(\text{OH})_6]\text{H}_2$, $[\text{SbO}_6]\text{H}_7$, $[\text{TeO}_6]\text{H}_6$, $[\text{IO}_6]\text{H}_5$, $[\text{Pt}(\text{OH})_6]\text{H}_2$. In the cases of antimonie, telluric and periodic acids, the effective basicity of the acid may be variable, depending on the nature and ionic volume of the relevant cation. In the same way, the amphoteric metallic hydroxides and amides in their acid function are to be regarded as hydroxo- or amido-complexes, the zincates, for example, being $\text{X}_2[\text{Zn}(\text{OH})_4]$.
- (c) The weak acids formed from the amphoteric metals of Groups Va and VIa of the Periodic Classification are characterized by the ease with which they condense to form anions containing several molecules of the acid anhydride. Thus, in the case of molybdenum, the molybdates in alkaline solution are represented by the formula R_2MoO_4 , but in acid solutions the formation of more complex anions takes place, and in the older literature the preparation of salts $\text{R}_2\text{O} \cdot n\text{MoO}_3 \cdot aq$ has been described, in which $n = 1, 2, 2.4, 3, 4, 8, 10$ and 16 , according to the acidity and concentration of the solutions.

Such condensed acids, containing only one type of acid anhydride, are known as *isopoly-acids*. The same acid anhydrides have the power of condensing with other acids—*e.g.* phosphoric or silicic acids—to form *heteropoly-acids*. Silicic acid itself, while tending to

form solid silicates derived from highly condensed anions, cannot be ranked amongst the isopoly-acids, but must stand in a class by itself, since—as will be seen in later sections—the structures of the silicates follow an entirely different plan from the structures of the iso- and heteropoly-acids.

THE HETEROPOLY-ACIDS

Historically, the theory and classification of the isopoly-acids has followed, and been based upon, the theory of the heteropoly-acids. It is therefore convenient to discuss these compounds first, and to deal with the isopoly-acids in the light of recent work.

The heteropoly-acids are formed by the union of varying numbers of acid anhydride molecules—most commonly WO_3 , MoO_3 or V_2O_5 —with a second acid which must be regarded in modern theory as furnishing the central atom or central ion of the whole complex anion. The power of functioning as the central atom in poly-acids is widely spread amongst the acidic and amphoteric elements, and even amongst the true metals, as is shown by Table 1.

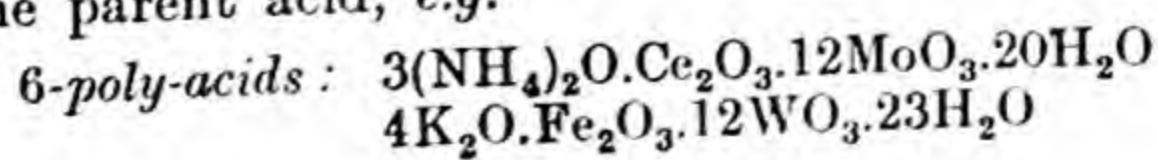
Table 1

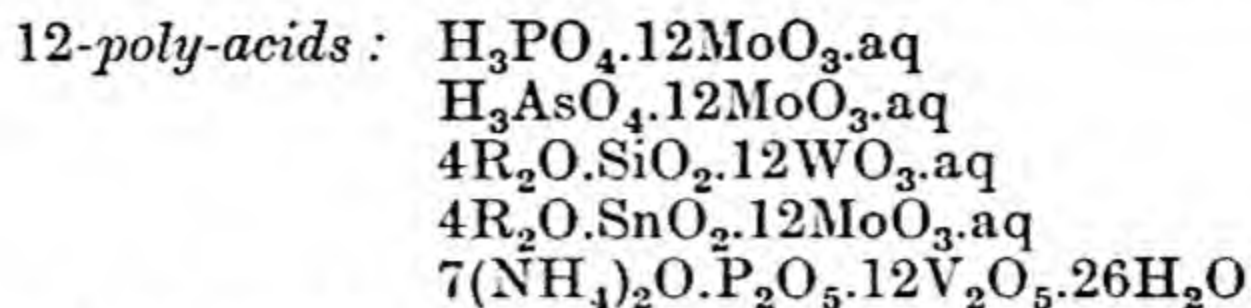
Elements Capable of Acting as Central Atom in Poly-acid Formation

Group I	H, Cu
Group II	Be
Group III	B, Al
Group IV	C, Si, Ge, Sn, Ti, Zr, Ce, Th
Group V	N, P, As, Sb, V, Nb, Ta
Group VI	Cr, Mo, W, U, S, Se, Te
Group VII	Mn, I
Group VIII	Fe, Co, Ni, Rh, Os, Ir, Pt

The salts of the poly-acids are obtained, in general, from solutions of the components, acidified to an appropriate hydrogen ion concentration. The less stable poly-acids may be decomposed by water; all are progressively degraded by hydroxyl ions, and are completely decomposed by strong alkalis.

Varying numbers of WO_3 , MoO_3 or V_2O_5 molecules may be combined with the parent acid—e.g. 8.5, 9, 10.5, 11 and 12 WO_3 per PO_4^{3-} ion in the tungstophosphates. There are, however, two types which are of particular importance for the theory of the poly-acids by virtue of their frequent recurrence. These are the acids with six and twelve MoO_3 , WO_3 or $\frac{\text{V}_2\text{O}_5}{2}$ groups, respectively, to each anion of the parent acid, e.g.



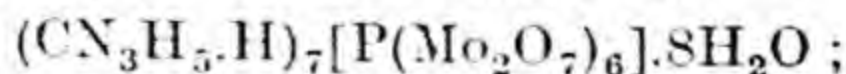


This preferential combination with 6 or 2×6 molecules of acid anhydride led to the classification of the poly-acids under an extension of the Werner theory, as developed successively by Miolati, Copaux and Rosenheim.¹ On the Rosenheim theory, the poly-acid formed from an element X (of valency n) as central atom is derived from a hypothetical form $\text{H}_{12-n}[\text{XO}_6]$ of the parent acid. The oxygen atoms of this complex may be replaced partially or wholly by acid radicals—*e.g.* MoO_4 —or by pyro-acid radicals— Mo_2O_7 . In this way, two ‘limiting series’ may be formulated— $\text{H}_{12-n}[\text{X}(\text{MoO}_4)_6]$ and $\text{H}_{12-n}[\text{X}(\text{Mo}_2\text{O}_7)_6]$. 6-poly-acids relegated by Rosenheim to this type are formed, for example, when X is I, Te, Fe, Cr, Al, Co, Ni, Rh, Cu, Mn and H_2 ; 12-poly-acids by P, As, Si, Ti, Ge, Sn, Zr, Th, Ce, B and H_2 (Table 2).

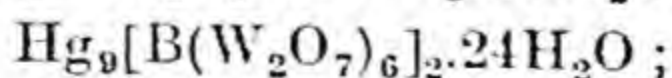
Table 2
Rosenheim's Formulation

Central atom	Valency	Parent acid	Heteropoly-acids
I	7	$\text{H}_5[\text{IO}_6]$	$\text{H}_5[\text{I}(\text{MoO}_4)_6]$
Te	6	$\text{H}_6[\text{TeO}_6]$	$\text{H}_6[\text{Te}(\text{MoO}_4)_6]$
P	5	$\text{H}_7[\text{PO}_6]$	$\text{H}_7[\text{P}(\text{Mo}_2\text{O}_7)_6]$
Si	4	$\text{H}_8[\text{SiO}_6]$	$\text{H}_8[\text{Si}(\text{Mo}_2\text{O}_7)_6]$
B	3	$\text{H}_9[\text{BO}_6]$	$\text{H}_9[\text{B}(\text{W}_2\text{O}_7)_6]$

It follows as a natural consequence of the Rosenheim theory that the poly-acids should exhibit very high basicities, although the maximum permitted basicity is very rarely reached—this is the case, for example, in the guanidinium salt



in the silver 10-molybdophosphate $7\text{Ag}_2\text{O}.\text{P}_2\text{O}_5.20\text{MoO}_3.24\text{H}_2\text{O}$, which Rosenheim formulates as $\text{Ag}_7\left[\text{P}(\text{Mo}_2\text{O}_7)_5\right].12\text{H}_2\text{O}$; in the 12-tungstoborate $18\text{HgO}.\text{B}_2\text{O}_3.24\text{WO}_3.24\text{H}_2\text{O}$ or



¹ A very full discussion of poly-acids from this standpoint is given by Rosenheim in Abegg's *Handbuch*, Vol. 4, Part 1, ii, pp. 977–1065 (1921).

and in the 10-tungstosilicate $4\text{BaO} \cdot \text{SiO}_2 \cdot 10\text{WO}_3 \cdot 22\text{H}_2\text{O}$ or $\text{Ba}_4\left[\text{Si}(\text{W}_2\text{O}_7)_5\right] \cdot 22\text{H}_2\text{O}$ obtained by Marignac. In general, the salts of the poly-acids can be fitted into Rosenheim's scheme only as acid salts. Since the salts are mostly heavily hydrated, retaining a portion of the water strongly, such a view is not incompatible with the chemical evidence. Copaux showed that the 'favoured' basicity is usually four less than the maximum permitted by the formula.

A close similarity in physical and chemical properties exists between the 6-heteropoly-acids and the so-called paratungstates and paramolybdates on the one hand, and between the 12-heteropoly-acids and the metatungstates and metamolybdates on the other. Thus, salts of metatungstic acid show the same great crystallizing power and the same crystal habit as the 12-tungstosilicates, -phosphates or -borates, the similarity extending even to identity of crystal cell dimensions. Chemically, the same similarity is shown by their great solubility in solvents containing oxygen—water, alcohol or ether—by the formation of etherates, which are probably ill-defined oxonium salts, by the property of coagulating albumen, and by the formation of very insoluble alkaloid salts. To account for these close relationships, Copaux brought the isopoly-acids into the Miolati-Rosenheim scheme as derivatives of hypothetical 'aquates', $\text{R}_{10}[\text{H}_2\text{O}_6]$. Thus, metatungstic acid would be $\text{H}_{10}[\text{H}_2(\text{W}_2\text{O}_7)_6] \cdot \text{aq}$. In the same way, the 6-poly-acids closely resemble paratungstic and paramolybdic acids, especially in the ease with which they are degraded directly to normal tungstates and molybdates, R_2WO_4 and R_2MoO_4 , by hydroxyl ions. According to Rosenheim, for example, the 6-molybdo-aluminates and chromites, $3\text{R}_2\text{O} \cdot \text{M}_2\text{O}_3 \cdot 12\text{MoO}_3 \cdot 20\text{H}_2\text{O}$, are strictly analogous to the complex oxalates $\text{R}_3[\text{M}(\text{C}_2\text{O}_4)_3]$ formed by these metals, in that the resulting complex shows the basicity of the parent acid, and is but loosely bound together, so that it shows all the reactions of the molybdate ion.

Although the Rosenheim theory served its purpose in collating and classifying the large number of heteropoly-acid derivatives which have been prepared, it remains essentially hypothetical and without experimental foundation. In particular, the important class of 12-poly-acids is based upon the assumption of $\text{Mo}_2\text{O}_7''$ and $\text{W}_2\text{O}_7''$ ions. There is no evidence at all of the existence of such ions, except the analogy of the dichromates, and alkaline degradation does not follow the course which the existence of pyrotungstate or pyromolybdate ions would presuppose. Moreover, the observed basicities of the acids, the amounts of constitutional water found,

and the revised formulation of the polyvanadate complexes (see below) can be reconciled with the theory only with difficulty. Modern work has therefore proceeded along two main lines: a study of the aggregation and degradation processes leading to poly-acid formation, and the application of the stereochemical structural principles which have been derived from crystallographic chemistry. It is still difficult to combine the results of these two approaches into one self-consistent explanation of the facts.

The Mechanism of Poly-anion Formation.—A variety of physico-chemical methods has been employed in studying the processes of aggregation and degradation in iso- and heteropoly acids. These methods include, especially, the direct determination of the ionic weights of the various species formed, cryoscopic measurements of the changes in the number of ions as each step in the aggregation takes place, and determination of the stoichiometry of the condensation reactions, which involve hydrogen ions. It is true to say that not one system has as yet been properly elucidated, but certain basic chemical principles underlying the formation of poly-acids are now probably understood.

The systematic study of the condensation reactions, and the recognition of their very general character, is due largely to G. Jander and his school.² Their work has been based largely on the attempt to measure ionic weights directly, by measuring the rate of diffusion of ions, in the presence of a large excess of an inert electrolyte (usually NaNO_3) to provide a uniform ionic atmosphere. It is then assumed that the observed diffusion coefficient D is related to the molecular or ionic weight, M , by an expression of the same form as Graham's law, namely that $D \cdot z \cdot \sqrt{M} = \text{constant}$, where z = the specific viscosity of the solution (i.e. $z = \eta_{\text{soln.}}/\eta_{\text{H}_2\text{O}}$). However, it has become clear that such diffusion measurements cannot furnish very precise quantitative data, and that the results must always be considered in conjunction with other evidence. In particular, the simple form of diffusion law, applied to solutions by Riecke (1890), cannot be strictly true for the diffusion of molecules of a solute, though it is valid for colloidal particles. A solution is a highly condensed system in which the size and effective shape of a diffusing molecule, and the magnitude of the charge on an ion, undoubtedly enter to some extent into the diffusion coefficient. Furthermore, the measurements are necessarily relative; they involve comparison of diffusion rates with some ion of known ionic weight. It is therefore necessary to make assumptions about the degree of hydration and effective diffusing mass of the reference ion, and also about the degree of hydration of the poly-acid anions themselves. All these

² For summaries see *Kolloid Beihefte*, 1934, 41, 1, 297; 1942, 54, 1.

factors restrict the usefulness of diffusion measurements, and Jander's work has been criticized accordingly.³ None the less, it makes a substantial contribution to the present status of the subject. It is more rapid, and experimentally simpler, to measure dialysis coefficients, rather than diffusion coefficients. This has been done by Brintzinger⁴ and by Jander,⁵ with results that accord in general with diffusion measurements. However, the interpretation of dialysis measurements is free from none of the criticisms applied to diffusion, and the properties of the membrane can introduce an additional uncertainty.

Nevertheless, the evidence obtained from diffusion measurements is of more than qualitative significance. The results obtained for

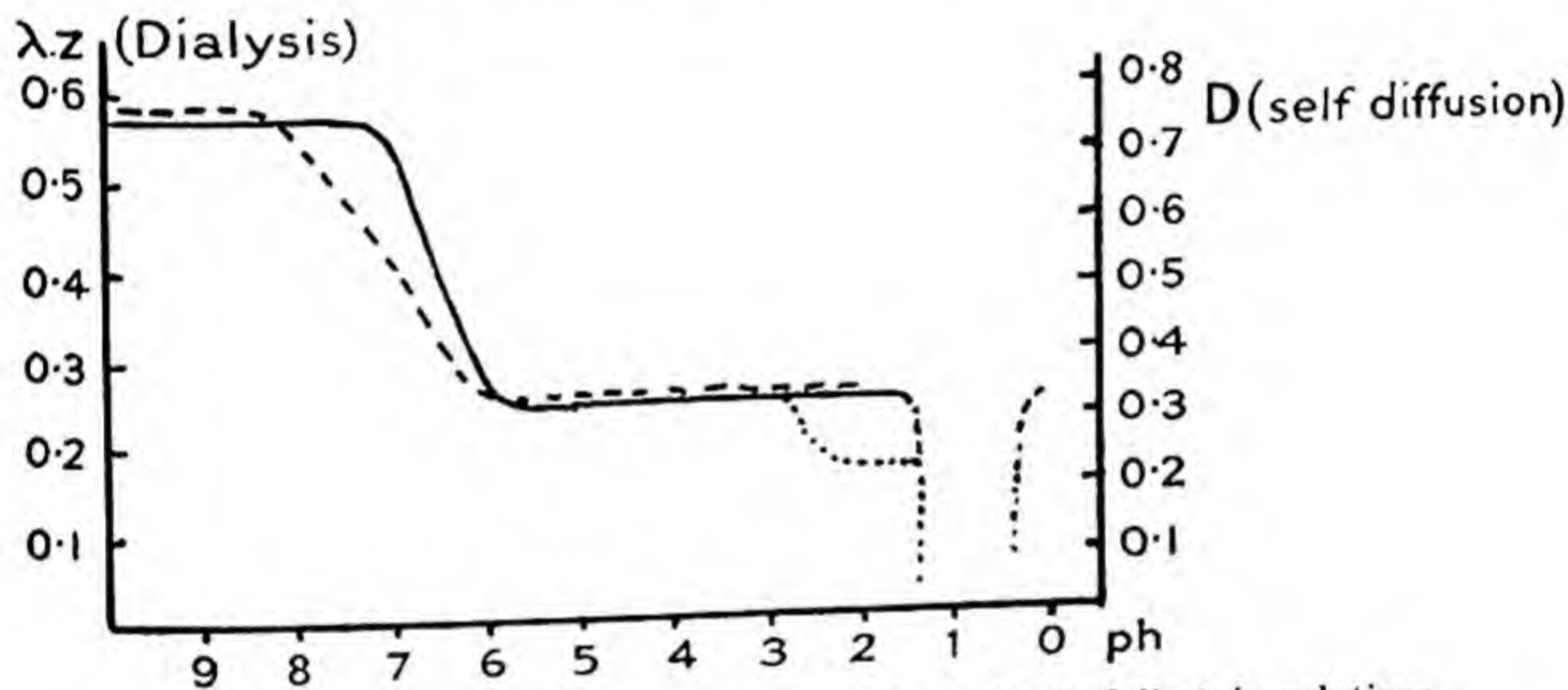


FIG. 32.—Dialysis and self-diffusion coefficients (dashed line) in solutions of sodium tungstate.

isopoly-acid systems are typified by Fig. 32. This relates specifically to tungstate solutions, but the behaviour of the molybdates and vanadates is essentially similar. The diagram combines the results of free diffusion and dialysis experiments,⁶ and of measurements of self-diffusion in tungstate solutions, made by a radioactive tracer method.⁷ In the former, although the hydrogen ion concentration is uniform throughout, diffusion takes place along a concentration gradient, and all reversible equilibria must be affected thereby. In the self-diffusion process, the measurements relate to the mobility of 'labelled' tungstate anions in a chemically uniform

³ P. Souhay, *Bull. Soc. Chim. France*, 1947, 14, 914.

⁴ *Z. anorg. Chem.*, 1935, 224, 97.

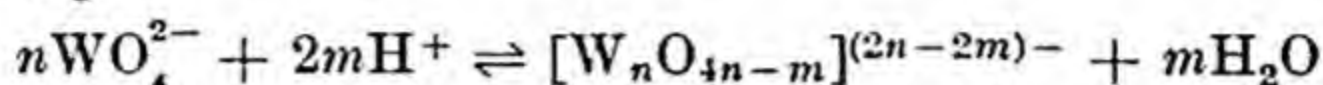
⁵ Jander and Spandau, *Z. phys. Chem.*, 1939, 185, 325; 1941, 188, 65.

Jander and Exner, *Z. phys. Chem.*, 1942, 190, 195.

⁶ Jander and Exner, *loc. cit.*, ref. 5.

⁷ K. Saddington and J. S. Anderson, *J.C.S.*, 1949, S381.

environment, in complete equilibrium at every point. Increase in the hydrogen ion concentration has the effect upon the diffusion coefficient seen in Fig. 32. In general, there are ranges of hydrogen ion concentration over which a uniform diffusion coefficient implies that practically all the tungstate anions are present in one state of aggregation. Transition from one state of complexity to another takes place, over one or two units of pH , at a hydrogen ion concentration determined by the equilibrium constant of a condensation reaction—*e.g.*



According to the numerical data of Jander and Exner, the dialysis coefficient has a steady value between pH 14 and pH 8. It then drops to a second steady value, which persists in dilute tungstate solutions from pH 6 to pH 1.5. In concentrated solutions there is some disputable evidence for a second transition, shown dotted on the diagram. At some hydrogen ion concentration close to pH 1 the iso-electric point is reached. Such solutions are unstable, give low and variable diffusion coefficients, and deposit precipitates of tungstic acid more or less rapidly. However, at still higher hydrogen concentrations it is possible to obtain solutions (albeit metastable) in which the diffusion coefficients rise once more, evincing evidence for the presence of ionic-disperse tungsten compounds.⁸

The physical process operative throughout these changes is the progressive aggregation of negative ions (by elimination of water), as their negative charges become neutralized by hydrogen ions. Only the first few stages in this process lead to the formation of stable species, existing over any wide range of conditions and capable of isolation in the form of crystalline salts. As the ratio of ionic weight to ionic charge increases, the potential of the ions falls, and aggregation is increasingly favoured. There is then a rapid change over from the conditions under which poly-anions are stable to those favouring negative colloids. Finally, at the iso-electric point, the ratio becomes infinite, and precipitation occurs. If the iso-electric point is passed, the charge may change sign, and complex cations may even be formed, with consequent degradation to the ionic-disperse state.

Diffusion measurements reveal quite unambiguously the existence, in stable solution, of successive distinct stages of condensation. The approximate degree of condensation at each stage can be deduced, but for the reasons mentioned earlier it is not always possible to distinguish between alternative interpretations of the

⁸ Cf. E. Buchholz, *Z. anorg. Chem.*, 1940, 244, 149, 168.

reactions. The values obtained for the ionic weight, calculated from Riecke's equation, are sensitive to the assumptions made about the reference ion (*see above*), so that whilst it is certain that there is no evidence for the existence of a $W_2O_7^{2-}$ ion (*cf.* $Cr_2O_7^{2-}$), the species existing in acid solutions might be either a 6- or 7-fold aggregate. Jander considers that another species of approximately twice the ionic weight is present in concentrated solutions more acid than $pH3$. To carry interpretation of the results further it is necessary to consider briefly the chemistry of the tungstates and molybdates.

The known metallic molybdates and tungstates, classified in the older literature simply according to the ratio of MoO_3 (or WO_3) to metallic oxide, give the impression that a large number of poly-acids must exist. However, the ratios $R_2O : XO_3$ give no direct information about the true molecular complexity, and the number of distinct poly-acids is, in fact, much less than might be inferred. As has been indicated, the species of anions existing in the solutions depends on the hydrogen ion concentration. Hence it is likely that, over the pH range characterized by a constant diffusion coefficient, the salts crystallizing in stable equilibrium will be based on a common condensed anion. Variations in the $R_2O : XO_3$ ratio may still arise, through the formation of acid salts; little is as yet known about the neutralization curves of the free poly-acids. Many of the salts contain constitutionally bound water, which cannot be removed without decomposition. It is, however, by no means impossible that some of the compounds which have been prepared represent metastable species, and do not correspond to the poly-anions predominating in the solutions from which they crystallize. There is also a serious analytical difficulty—that alternative modes of formulating the salts (especially the salts of the alkali metals) differ so little in composition that, in the absence of the most precise analytical work, it is not possible to decide unambiguously between them.

The Molybdates.—The metallic molybdates described in the literature^{9, 10} fall into the following nominal classes:

Normal molybdates, $R_2O, MoO_3.aq$. The alkali salts are obtained from neutral or alkaline solutions, and are but little hydrolysed. The K , Li and NH_4 salts may be obtained anhydrous.

Dimolybdates. The dimolybdates obtained from solution are all hydrated—*e.g.* $Na_2O.2MoO_3.4,5$ or $6H_2O$ —with a narrow range of

⁹ *Cf.* Jander, Jahr and Heukeshoven, *Z. anorg. Chem.*, 1930, **194**, 383.

¹⁰ H. Guiter, *Bull. Soc. Chim. France*, 1942, **9**, 622; *Compt. rend.*, 1943, **216**, 769; 1945, **220**, 146. G. Carpeni, *Bull. Soc. Chim. France*, 1947, **14**, 492.

stability about $pH 6$. They have usually, although quite arbitrarily, been formulated like the dichromates. Recent work¹¹ makes it doubtful whether they exist at all since some, at least, of the modes of preparation that have been described furnish mixtures of normal molybdates and paramolybdates. Anhydrous dimolybdates, such as $Na_2Mo_2O_7$, can be formed from melts,^{11a} but the ion $Mo_2O_7^{2-}$ does not exist as a discrete group. It exists within the crystal as an infinite-chain anion, of rather complicated structure,^{11b} which cannot pass into solution without being broken up into smaller units by a process of hydration.

Paramolybdates. These are the most stable polymolybdates in solution. Their saturated solutions have pH about 4.5. Klason¹² formulated them as if derived from $H_6[Mo_3O_{12}]$, Sand and Eisenlohr¹³ as if from $H_{10}[Mo_{12}O_{41}]$, and the weight of Rosenheim's work was for long taken as strong evidence for the formula $5R_2O.12MoO_3.aq$ ¹⁴—e.g. $5Na_2O.12MoO_3.38H_2O$, with $Na_2O : MoO_3 : H_2O = 1 : 2.40 : 7.60$. However, the alternative formulation $3R_2O.7MoO_3.aq$ (leading to $3Na_2O.7MoO_3.22H_2O$, with $Na_2O : MoO_3 : H_2O = 1 : 2.33 : 7.33$), suggested earlier by Delafontaine,¹⁵ is equally in accord with the analytical data. The true formula is discussed below.

Trimolybdates, $R_2O.3MoO_3.aq$, are formed by saturating alkalis with molybdic oxide, and their saturated solutions have $pH = 4.4$. They crystallize also from paramolybdate solutions in the presence of acetic acid.

Metamolybdates, $R_2O.4MoO_3.aq$, formed from concentrated solutions of alkali molybdates treated with 1.5 molecules of hydrochloric acid. All are hydrated, retaining some water even above 120° .

Octomolybdates, $R_2O.8MoO_3.aq$, are formed from concentrated solutions of alkali molybdates with 1.75 molecules of hydrochloric acid. They form a heavily hydrated, well-crystallized isomorphous series, but readily lose their crystal water with simultaneous decomposition. On Rosenheim's theory, both meta- and octomolybdates were regarded as salts of the 12-molybdic acid $H_{10}[H_2(Mo_2O_7)_6]$.

Decamolybdates, $R_2O.10MoO_3.aq$, from concentrated alkali molybdates and hydrochloric acid. Unlike the meta- and octomolybdates, they have little power of coagulating albumen. It may also be significant that $(NH_4)_2O.10MoO_3.4H_2O$ is described as yellow,¹⁰ whereas the polymolybdates proper are colourless.

¹¹ I. Lindqvist, *Nova Acta Reg. Soc. Sci. Upsala*, 1950 (iv), 15, No. 1.

^{11a} F. Hoermann, *Z. anorg. Chem.*, 1928, 177, 145.

^{11b} I. Lindqvist, *Acta Chem. Scand.*, 1950, 4, 1066.

¹² *Ber.*, 1901, 34, 153.

¹³ *Z. anorg. Chem.*, 1907, 52, 68, 87.

¹⁴ *Z. anorg. Chem.*, 1916, 96, 141.

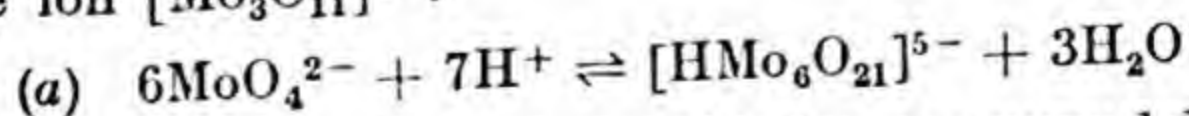
¹⁵ *J. prakt. Chem.*, 1865, 95, 141.

Lindqvist^{11, 19} has established fairly conclusively that the meta-molybdates and octomolybdates are all derived from an octomolybdic acid, $H_4[Mo_8O_{26}]$, although more highly condensed molybdate anions also probably exist in the form of their salts, and may be contained in the decamolybdates, 16-molybdates, etc.

Condensation equilibria in molybdate solutions, as shown by diffusion measurements, are closely similar to those illustrated in Fig. 32. There is evidence for, at most, two condensed anions in the solutions: an anion assigned an ionic weight of about 900, and interpreted by Jander as a hexamolybdate ion, and perhaps, although not certainly, an anion of about twice this complexity, between pH 1.5 and pH 1.0.

The formation of the paramolybdates can clearly be associated with the existence of the 6- or 7-fold polymolybdate ion between pH 6 and pH 1.5. There is now no doubt that the paramolybdates are heptamolybdates, with the anion $[Mo_7O_{24}]^{6-}$. Garelli and Tettamanzi¹⁶ prepared mixed paramolybdates of ammonium and triethanolamine, affording distinct analytical evidence in favour of the older heptamolybdate formula. More recently, Lindqvist¹⁷ has made very precise complete analyses of sodium and ammonium paramolybdates, using the powerful new separation techniques afforded by ion exchange processes, with results that significantly point to the formula $R_6[Mo_7O_{24}].aq.$ This conclusion is, in any case, confirmed beyond doubt by X-ray measurements of the cell dimensions and density of ammonium paramolybdate. In atomic weight units, the contents of the unit cell weigh 4958 ± 20 , which corresponds to $M = 1240 \pm 5$ on the probable assumption of four molecules per unit cell. Rosenheim's formula, $(NH_4)_5H_5[H_2(MoO_4)_7].H_2O$, has $M = 1057$, and the heptamolybdate formula, $(NH_4)_6[Mo_6O_{24}].4H_2O$, has $M = 1236$. Only the latter is compatible with the experimental results.¹⁸

The formula of the crystalline paramolybdates is thus established. It still remains to be shown that the anion $[Mo_7O_{24}]^{6-}$ exists as such in the solution. Jander considered that conductometric titrations indicated that a hexamolybdate ion was formed according to equation (a), perhaps through the intermediate formation of a trimolybdate ion $[Mo_3O_{11}]^{4-}$.



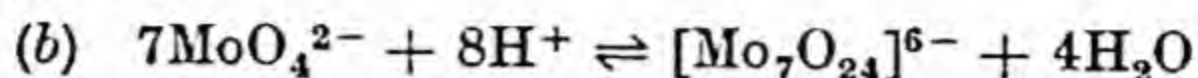
The formation of paramolybdate would thus consume 1.167 H^+ ions per MoO_4^{2-} ion, or 58.3 per cent of the total acid equivalent to the

¹⁶ *Atti Acad. Sci. Torino*, 1935, 70, 382; *Chem. Abs.*, 1935, 29, 7864.

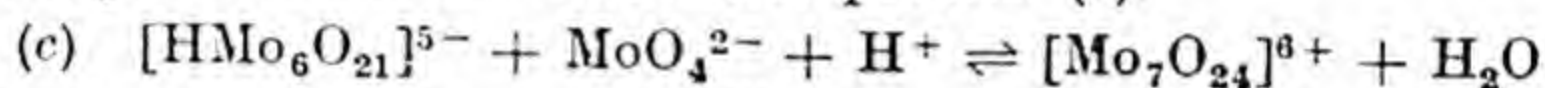
¹⁷ *Acta Chem. Scand.*, 1948, 2, 88.

¹⁸ J. Sturtevant, *J. Amer. Chem. Soc.*, 1937, 59, 630.

molybdate. The alternative reaction (b) requires 1.143 H^+ ions per MoO_4^{2-} ion, or 57.1 per cent of the total acid for neutralization. The results of conductometric titrations cannot distinguish between these alternatives.



Byé¹⁹ has examined the stoichiometry of this stage of the condensation by the method of 'thermometric titration', a cryoscopic procedure in which a solution of sodium molybdate in fused $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} + \text{Na}_2\text{SO}_4$, at its transition temperature, is titrated with sulphuric acid. Under these circumstances the change in depression of the transition temperature reflects directly the change in the number of anions as condensation takes place. According to Byé, the results are sufficiently precise and reproducible to distinguish significantly between processes (a) and (b), in favour of the latter. However, this is still an open question. It is not impossible that, as supposed by Jander, the predominant species in solution is the hexamolybdate ion, but that the paramolybdates are the product of the additional process (c).



Although, in solution, the equilibrium may lie far to the left-hand side, it could be shifted in favour of the heptamolybdate ion at the surface of the growing crystal.

If it may be concluded that the constitution of the paramolybdates has been established, the di-, tri- and tetramolybdates should be capable of formulation as acid paramolybdates. It is not certain that such a conclusion can be harmonized with the analytical evidence, and it may be that some of these are, in fact, derived from hexamolybdate or octomolybdate anions. The constitution of the compounds richer in MoO_3 is obscure. Byé's work affords no evidence for the formation of 12-molybdate anions, and in view of the fact that the iso-electric point of molybdic acid is at $\text{pH} = 0.9$,²⁰ it is possible that the yellow decamolybdates, at least, are molybdenyl compounds, containing cationic molybdenum in the form of $[\text{MoO}_2]^{2+}$ or $[\text{MoO}]^{4+}$ groups.

The Tungstates.—As with the molybdates, numerous tungstates of the metals have been described, differing in their $\text{R}_2\text{O} : \text{WO}_3$ ratios. Of these, however, three classes stand out as well defined and of the greatest importance: the normal tungstates, R_2WO_4 , crystallizing from alkaline solutions, the paratungstates, $5\text{R}_2\text{O} \cdot 12\text{WO}_3 \cdot \text{aq}$ or $3\text{R}_2\text{O} \cdot 7\text{WO}_3 \cdot \text{aq}$, crystallizing from weakly acid solutions, and the metatungstates, $\text{R}_2\text{O} \cdot 4\text{WO}_3$, formed by

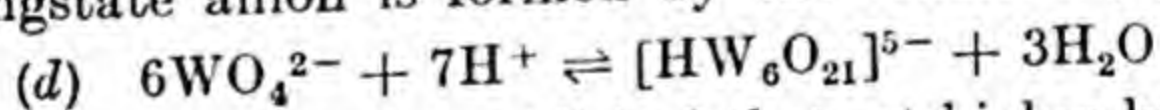
¹⁹ *Bull. Soc. Chim. France*, 1942, 9, 517.

²⁰ G. Carpeni, *Bull. Soc. Chim. France*, 1947, 14, 496.

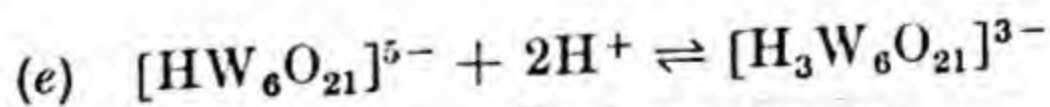
dissolving tungstic acid in sodium tungstate and also, under specified conditions, from strongly acidified solutions of Na_2WO_4 . Copaux²¹ showed that the metatungstates are isomorphous with the phosphotungstates and silicotungstates—i.e. with the typical 12-heteropoly acids. Hence they are undoubtedly to be represented as $3\text{R}_2\text{O} \cdot 12\text{WO}_3 \cdot \text{aq}$.

The paratungstates, however, are not isomorphous with the paramolybdates, and it cannot be assumed that they should be represented by analogous formulæ. Cogent evidence, based on careful analytical work, has recently been advanced to show that the ratio $\text{Na}_2\text{O} : \text{WO}_3$ in sodium paratungstate is 1:2.40, as required by $5\text{Na}_2\text{O} \cdot 12\text{WO}_3 \cdot 28\text{H}_2\text{O}$.^{22, 23} It is evident from Fig. 32 that, over the wide range of conditions under which solid paratungstates may be in equilibrium with the solution, the latter contains a 6- or 7-fold condensed tungstate anion. X-ray measurements²² of the triclinic crystals of sodium paratungstate show that the weight of the unit cell is not compatible with the formula $3\text{Na}_2\text{O} \cdot 7\text{WO}_3 \cdot 16\text{H}_2\text{O}$, but would represent just two molecules of $5\text{Na}_2\text{O} \cdot 12\text{WO}_3 \cdot 28\text{H}_2\text{O}$. However, since the diffusion measurements point to an ionic weight of 1300–1500, the ion in solution cannot be a 12-tungstate ion. It may probably be inferred that the unit cell of the crystal contains four molecules of $\text{Na}_5\text{H}[\text{W}_6\text{O}_{21}]$ and 54 molecules of water, two molecules of water being constitutional.

This formulation of the paratungstate ion is borne out by the physicochemical studies of the condensation reaction, in which Souchay²⁴ confirms the views of Jander and Heukeshoven,²⁵ that the paratungstate anion is formed by the reaction (d).



It has also been fairly well established that, at higher hydrogen ion concentrations, a further reaction ensues, involving two H^+ ions per hexatungstate ion. Unlike reaction (d), this is a slow process, and is in part responsible for the change in properties, or ageing, of acidified tungstate solutions. Since, as the diffusion and cryoscopic measurements show, the molecular complexity does not undergo change through this process, the reaction can only be represented²⁶ as (e).



²¹ *Ann. Chim. Phys.*, 1909, 17, 217; 1912, 25, 22.

²² K. Saddington and R. Cahn, *J.C.S.*, 1950.

²³ R. H. Vallance, *J.C.S.*, 1931, 1421; P. Souchay, *Ann. Chim.*, 1943, 18, 61.

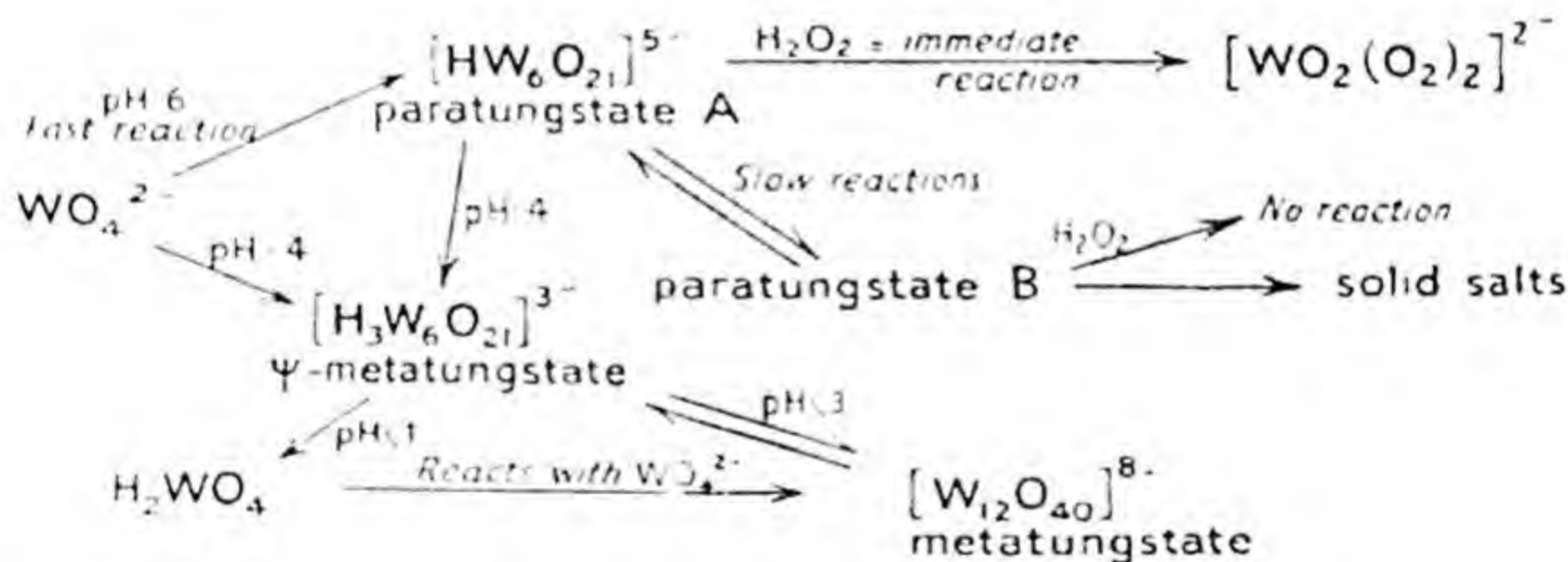
²⁴ *Ann. Chim.*, 1943, 18, 61.

²⁵ *Z. anorg. Chem.*, 1930, 187, 60.

²⁶ P. Souchay, *Ann. Chim.*, 1943, 18, 169.

The product $[\text{H}_3\text{W}_6\text{O}_{21}]^{3-}$, called by Souchay the pseudo-metatungstate ion, is to be regarded as structurally distinct from the paratungstate ion, and not merely as an intermediate stage in the dissociation of a fairly weak acid. Since it persists—in moderately dilute solutions, at least—up to fairly high hydrogen ion concentrations, it is probably this species which reacts with other acids to form the heteropoly-tungstates.

The reactions given are, however, still inadequate to explain fully the properties of solutions within the paratungstate range. Whereas solutions freshly acidified to pH 6 react instantly with hydrogen peroxide, aged solutions, or solutions freshly made from crystalline paratungstate, react only slowly.²⁷ Souchay²⁴ considers that this implies an equilibrium in solution between two species of hexatungstate ions, which may differ structurally or in respect of hydration: 'paratungstate A', formed by a rapid reaction between WO_4^{2-} ions and H^+ ions, is itself reactive towards hydrogen peroxide, hydrogen ions, etc.; 'paratungstate B' is the anion present in the crystalline salts, and reacts in solution through its intermediate conversion to paratungstate A.



It is still uncertain whether the hexatungstate ions and metatungstate ions are inter-convertible, as supposed by Jander, since it has been stated²⁶ that the $[\text{W}_{12}\text{O}_{40}]^{8-}$ ion is stable in solution up to pH 6, and probably degrades directly to the simple tungstate ion. The conditions under which metatungstates are prepared are generally such that reaction could take place between free tungstic oxide hydrate, transiently formed, and some one of the species present in solution.

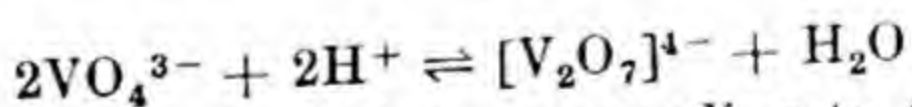
The reactions occurring in tungstate solutions are thus more complicated than could be inferred from the application of any one physicochemical technique: it is possible that a similar complexity in molybdate solutions is masked by a greater lability. It has

²⁷ K. F. Jahr, *Naturwiss.*, 1941, 29, 510.

always to be borne in mind that the stoichiometric equations such as (b) and (d) do not represent the actual chemical mechanism of the reactions. These must proceed by kinetically simple steps, probably involving successive reactions with the simple ions present in extremely low equilibrium concentrations in the presence of the condensed anions. Slow ageing processes, and isolation of salts not derived from the dominant species of poly-acid present in the solution, can both be regarded as consequences of the complexity of the true mechanism.

The Polyvanadates.—If no finality has been reached as to the constitution of the tungstate and molybdate systems, the chemistry of vanadic acid is still more obscure. It has long been known that vanadates of the alkali metals and of silver exist, with the ratio $R_2O : V_2O_5 = 3 : 1$, $2 : 1$ and $1 : 1$, analogous to the ortho-, pyro- and meta-phosphates. This similarity is essentially formal, however; whereas the phosphoric acids represent successive stages in the hydration of phosphorus pentoxide, and the poly-phosphoric acids are irreversibly hydrolysed to orthophosphate in solution, the vanadic acids are related by reversible equilibria, which are shifted by changes in hydrogen ion concentration. They must be regarded as successive stages in a condensation process that culminates in the precipitation of V_2O_5 . This process recognizably proceeds beyond the stage of metavanadate. When acids are added to the colourless solution of sodium vanadate, Na_3VO_4 , a transient brownish red colour is developed, which passes over into a yellow-orange. Since the pH of such acidified solutions takes time to attain a steady value, it is evident that reaction proceeds by way of some unstable intermediate compound. Salts with various ratios $R_2O : V_2O_5$ have been isolated from such acidified solutions.²⁸

Düllberg,²⁹ from a comprehensive early study of the system, concluded that divanadates, trivanadates and hexavanadates were formed in turn. It is agreed that the first reaction, occurring about pH 11, is



Diffusion data³⁰ indicate that, corresponding to the formation of metavanadates and the orange polyvanadates, two further condensation processes take place at approximately pH 9 and pH 7 respectively. The metavanadates have been variously represented as $R_3[V_3O_9]$ ^{29, 31} and as $R_4[H_2V_4O_{13}]$.³⁰ The evidence is not decisive,

²⁸ Friedheim, *Ber.*, 1890, 23, 1530, 2600; *Z. anorg. Chem.*, 1894, 5, 437; Rosenheim, *ibid.*, 1912, 98, 223.

²⁹ *Z. phys. Chem.*, 1903, 45, 129.

³⁰ Jander and Jahr, *Z. anorg. Chem.*, 1933, 212, 1.

³¹ P. Souchay and G. Carpeni, *Bull. Soc. Chim. France*, 1946, 13, 160.

but the first formula, which accords with the molecular weight found for the supposed esters of metavanadic acid, would lead to the formulation of the orange vanadates as $R_4[V_6O_{17}]$.³¹ A number of the salts isolated from acid vanadate solutions can be satisfactorily represented on this basis—*e.g.* $2Na_2O.3V_2O_5.16H_2O$ or $Na_4[V_6O_{17}].16H_2O$, $Na_2O.2V_2O_5.9\frac{2}{3}H_2O$ or $Na_3H[V_6O_{17}].14H_2O$.³² However, vanadates with $R_2O : V_2O_5 = 4 : 5$, $3 : 5$ and $2 : 5$ are well authenticated also,³³ and electrometric measurements³⁴ have been interpreted as requiring the formation of a pentavanadate ion, present as $[H_3V_5O_{16}]^{4-}$ in the orange solutions. Whilst the balance of evidence probably favours the hexavanadate formula for the species existing in acid solutions, direct evidence is lacking.

Beyond the iso-electric point of vanadium pentoxide (*pH* 1) there is no doubt that the formation of vanadyl cations, $[VO_2]^+$, takes place. It is highly probable that some compounds reported in the literature as vanadates, with light colour and high V_2O_5 content, actually contain cationic vanadium.

The Formation of Heteropoly-acids.—The work described in the foregoing sections provides some interpretation of the processes responsible for the formation of the isopoly-acids. It should be possible to extend the interpretation to those mixed solutions from which the salts of heteropoly-acids are obtained. Since these compounds are always prepared from acid solutions it would appear that phosphoric acid, silicic acid, etc., may react either with some pre-existing isopoly-acid anion, or with the small concentration of simple ions present in equilibrium with the isopoly-acids.

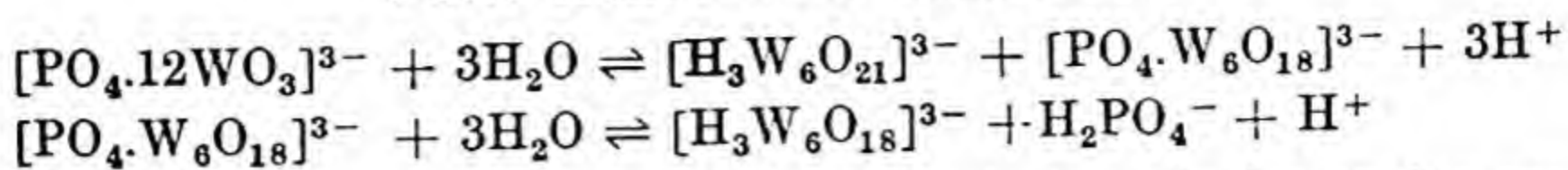
There is as yet not much evidence as to the constitution of heteropoly-acid solutions. Measurements of diffusion and dialysis³⁵ show quite definitely that, except perhaps in the most concentrated solutions, the anions of the 12-poly-acids are dissociated into species having about the same ionic weight as those present in pure molybdate or tungstate solutions at the same hydrogen ion concentration. There is agreement between Jander and Souchay that the formation and breakdown of, *e.g.*, the 12-tungstophosphate ion can be represented as a reaction between the phosphate ion and the pseudo-metatungstate ion, $[H_3W_6O_{21}.aq]^{3-}$. This probably implies that the only heteropoly-acid anion in the solutions is a 6-tungstophosphate ion which is not known in the form of any crystalline salts.

³² Rosenheim, Pieck and Pinsker, *Z. anorg. Chem.*, 1916, 96, 139.

³³ Jander and Jahr, *ibid.*, 1933, 211, 49.

³⁴ Britton and Robinson, *J.C.S.*, 1932, 1955; Britton and Welford, *J.C.S.*, 1940, 761.

³⁵ Jander and Witzmann, *Z. anorg. Chem.*, 1933, 214, 145; Jander, *Z. phys. Chem.*, 1940, 187, 149; Jander and Exner, *ibid.*, 1942, 190, 195.



Both of these equilibria would be shifted strongly by an increase in acidity, in accordance with the fact that the salts and the Drechsel ether complexes of the heteropoly-acids can be prepared only from strongly acid solutions.

The formation of poly-acids of the 1 : 6 series can evidently be fitted to the same scheme of reactions, as also can the so-called 1 : 9 acids, since these are generally considered to be properly represented by the doubled formula—*e.g.* $\text{Na}_6[(\text{PO}_4)_2.18\text{WO}_3].\text{aq.}$ However, the formation of the 1 : 11 (or possibly 2 : 22) series, typified by the salt $7\text{K}_2\text{O}.\text{P}_2\text{O}_5.22\text{WO}_3.\text{aq.}$ cannot be explained if the reactions involve only pre-existing hexatungstate units at each stage. The acids of this series have some importance, since it has been stated³⁶ that they are the first degradation products of 12-tungstophosphates and the other acids of the 1 : 12 type. If this is correct, it implies that the simple WO_4^{2-} and MoO_4^{2-} ions participate in the reactions.

The Structure of the Poly-acids.—The general conclusion to be drawn from the foregoing discussion is that the poly-acids are formed by a sequence of reversible reactions of the 'oxygen bridging' type encountered previously (Chapter VI). In this process of aggregation, the anions containing six atoms of molybdenum, tungsten, and possibly vanadium also, are noteworthy, as species of particular stability which may furnish structural units for direct incorporation in the crystals of the salts, or may undergo further processes of condensation. The physicochemical studies of the solutions afford no evidence that the $\text{M}_2\text{O}_7^{2-}$ ion, which plays a special role in the Rosenheim-Miolati theory, is at any time present in appreciable concentration. Nevertheless, this ion is undoubtedly a stage in the aggregation process.

The present conception of the structure of the poly-acids finds its historical origin in a theory of Pfeiffer³⁷ that complexes of high co-ordination number might be built about a central polyatomic ion, rather than about a central atom. Accepting the Rosenheim-Miolati view, that poly-acids were derived from hypothetical acids $\text{H}_{12-n}[\text{XO}_6]$, Pfeiffer suggested that WO_3 or MoO_3 molecules might be co-ordinated around the $[\text{XO}_6]$ ion in a second shell, giving, for example, $\text{H}_7[\text{PO}_6(\text{WO}_3)_{12}]$. The stereochemical conceptions which have emerged from the X-ray investigation of crystal structures have been applied along these same lines, first

³⁶ Malaprade, *Ann. Chim.*, 1929, 11, 104; Souchay, *ibid.*, 1945, 20, 73.

³⁷ *Z. anorg. Chem.*, 1918, 105, 26.

by Pauling, and then very successfully by Keggin, to the theory of the 12-poly-acids.

It has been shown, notably by W. L. Bragg and his school, that the structures of silicates and similar complex crystals can be built up of positive ions (*e.g.* Al^{3+} , Ca^{2+} , Si^{4+}) and negative ions (*e.g.* O^{2-} , OH^-), so arranged that each positive ion is surrounded by a

Table 3

Radius ratio = limiting R_A/R_B	Co-ordination number	Resulting geometrical configuration
—	2	linear
0.15	3	plane triangle
0.22	4	tetrahedral
0.41	4	square planar
0.41	6	octohedral
0.73	8	cubic

Table 4

Co-ordination Numbers of Ions in Oxides

Ion	Radius ratio	Goldschmidt co-ordination number	
		Predicted	Observed
B^{3+} . . .	0.20	3 or 4	3 and 4
Be^{2+} . . .	0.25	4	4
Si^{4+} . . .	0.37	4	4
Al^{3+} . . .	0.41	4 or 6	4 and 6
Mg^{2+} . . .	0.47	6	6
Ti^{4+} . . .	0.55	6	6
Sc^{3+} . . .	0.60	6	6
Mo^{6+} . . .	0.53	6	6
Zr^{4+} . . .	0.62	6	6 and 8

regular geometrical array of negative ions. The *co-ordination number* of the positive ion, in this crystallographic sense as conceived by V. M. Goldschmidt,³⁸ is dependent only on the ratio of the radius of the positive ion, R_A , to that of the negative ions, R_B (Table 3).

For the metallic ions, co-ordinated with oxygen, the Goldschmidt co-ordination numbers 4 and 6 predominate (Table 4), so that the

³⁸ *Ber.*, 1927, 60, 1263.

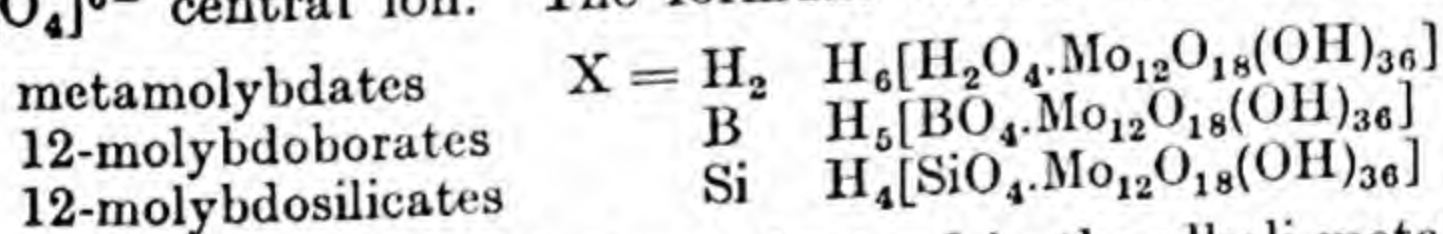
structures referred to may be built up from tetrahedra and octohedra of oxygen ions, so packed to share edges, corners or faces that the correct gross composition and the correct symmetry are obtained.

It follows from the data of Table 4 that there is room about an Mo^{6+} or W^{6+} ion for an octohedron of oxygen ions. Pauling³⁹ accordingly suggested that, in the 12-poly-acids, twelve such MO_6 octohedra are linked by each sharing three corners with neighbouring octohedra. Each then has three unshared corners. To saturate these, Pauling assumes that hydrogen ions are taken up (part of the crystal water being then constitutional), so that a stable, neutral $\text{M}_{12}\text{O}_{18}(\text{OH})_{36}$ group is formed (Fig. 33 (a) and (b); in Fig. 33 (b), the octohedra are represented diagrammatically by small circles).



FIG. 33.—The structure of the 12 tungstosilicate ion and related ions according to Pauling. Twelve distorted octohedra are combined by sharing corners in the manner shown, the resulting structure being linked together as shown diagrammatically in (b). The complete structure has the composition $(\text{SiO}_4\text{W}_{12}\text{O}_{18}(\text{OH})_{36})^{4-}$.

In the centre of the structure thus formed, there is room for a tetrahedral ion, XO_4 . The total basicity of the anion is then identical with that of the central atom, i.e. $8 - n$, where n is the valency of the atom X. Following Copaux and Rosenheim, Pauling then bases the metamolybdates and metatungstates upon a $[\text{H}_2\text{O}_4]^{6-}$ central ion. The formulæ arrived at are thus:

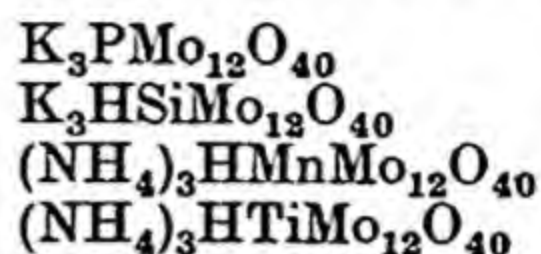
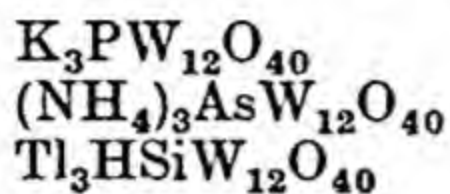


The basicities agree with those observed in the alkali metal salts. It follows, however, that no acid or salt should contain less than eighteen molecules of constitutional water; this is not in accord with the known facts. Thus, Scroggie and Clark⁴⁰ found that 12-tungstosilicic acid, dried at 100° , contained $8\text{H}_2\text{O}$ including the four ionizable hydrogen atoms, so that its total formula is $\text{H}_{16}\text{SiW}_{12}\text{O}_{46}$. Six molecules of this water, but not more, although

³⁹ *J. Amer. Chem. Soc.*, 1929, 51, 2868.

⁴⁰ *Proc. Nat. Acad. Sci.*, 1929, 15, 1; see also Rosenheim, *Z. anorg. Chem.*, 1934, 220, 73; Kahane, *Bull. Soc. Chim.*, 1931, [iv], 49, 557.

very firmly held, can be removed by dehydration without breaking down the poly-acid, giving a product, $\text{H}_4\text{SiW}_{12}\text{O}_{40}$, which must be regarded as the anhydrous acid. This form of anion, $[\text{RM}_{12}\text{O}_{40}]$, seems, indeed, to be the lowest form obtainable by dehydrating the 12-poly-acids generally. It is present also in those 12-heteropoly-acid salts which are obtainable in the anhydrous state—*e.g.*



The existence of this form of anion at once rules out both the Rosenheim and the Pauling theories, but it has been made the basis of a similarly conceived structure by Keggin. The real contribution made by Pauling was the idea that the anion of a poly-acid

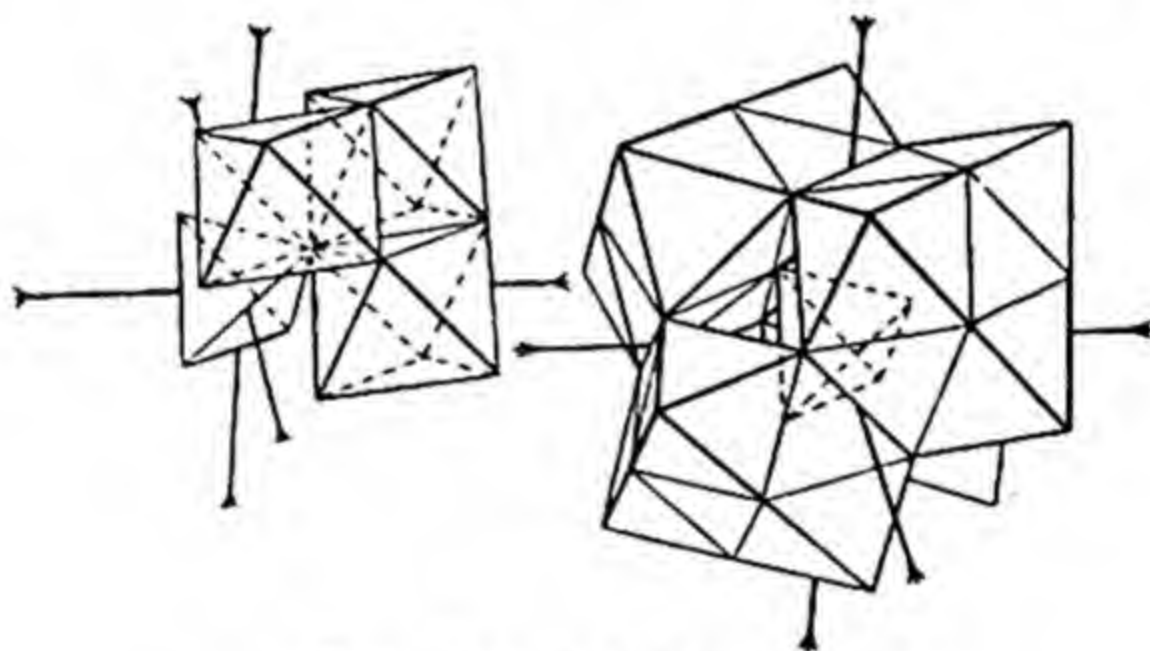


FIG. 34a and FIG. 34b.

can be regarded as a self-contained unit having the typical oxide co-ordination structure. The sharing of corners and edges between MO_6 octohedra is the characteristic basis upon which the trioxides MoO_3 , WO_3 and all the complex intermediate oxides of tungsten and molybdenum are constructed.⁴¹

Keggin,⁴² like Pauling, builds up the poly-acid anions on a co-ordination structure. A tetrahedral XO_4 ion at the centre is surrounded by MoO_6 or WO_6 octohedra. Each corner atom of the XO_4 group is shared with three octohedra (Fig. 34 (a)), each of which also shares one oxygen atom with each of its two neighbours. The four Mo_3O_{13} groups so obtained are linked together by sharing corners (Fig. 34 (b)), giving an anion $[\text{XM}_{12}\text{O}_{40}]^{8-n}$. The packing together of such anions in the crystal leaves large

⁴¹ A. Magneli, *Arkiv Kemi, Min., Geol.*, 1946, No. 24A; *Acta Chem. Scand.*, 1948, 2, 501.

⁴² *Proc. Roy. Soc.*, 1934, A, 144, 75.

spaces to be filled, thus permitting the existence of high hydrates—*e.g.* $\text{H}_3[\text{PW}_{12}\text{O}_{40}]\cdot 29\text{H}_2\text{O}$. This hydrate readily loses water down to $\text{H}_3[\text{PW}_{12}\text{O}_{40}]\cdot 5\text{H}_2\text{O}$. In the salts, the space occupied by three of these water molecules is taken by three cations, thereby accounting for the preferential formation of such salts as $\text{K}_3\text{H}[\text{SiMo}_{12}\text{O}_{40}]$, even where the complete replacement of hydrogen might be expected.⁴³

The outer cage of the Keggin structure is complete in itself, whether or not the four innermost oxygen atoms are shared also with some central XO_4 group. There is therefore no need for the artificial hypothesis that metatungstates are derivatives of some $[\text{H}_2\text{O}_4]^{6-}$ ion; metatungstic acid is properly to be represented as $\text{H}_8[\text{W}_{12}\text{O}_{40}]$.

This model of Keggin's has been very fully substantiated by the X-ray study of numerous 12-poly-acids and their salts,⁴⁴ so that the structure of these compounds can be considered as established with a high degree of probability. There is no published evidence for the structure of other series of poly-acids—*e.g.* those with 9, 10 or 11 MoO_3 or WO_3 for each central ion. It is probably permissible to regard them all as binuclear structures, sharing 6, 4 or 2 complete MO_6 octohedra between two anionic cages.⁴⁵

The same principles can be applied to the problem of the 6-poly-acids. On Rosenheim's formulation, the 6-poly-acids are of the type $\text{R}_n[\text{X}(\text{MO}_4)_6]$, in which the W^{6+} and Mo^{6+} ions are at the centres of tetrahedra of oxygen ions. As may be seen, however, from Table 6, and as is the case in the 12-poly-acids, the W^{6+} and Mo^{6+} ions must normally be in 6-fold co-ordination with oxygen. One geometrical arrangement which fulfils this condition for the $[\text{XM}_6\text{O}_{24}]$ group is that illustrated diagrammatically in Fig. 35, where six MO_6 octohedra are arranged in a hexagonal annulus, so as to share two corners with each of the two neighbouring octohedra.⁴⁶ The central cavity of the resulting $[\text{M}_6\text{O}_{24}]^{12-}$ structure just accommodates one octohedron, so that the remaining cation X^{n+} may be inserted in the same kind of 6-fold co-ordination. The basicity of the anion so formed is $12-n$ (where n = the valency of the element X), as on Rosenheim's formulation. An XO_6 octohedron thus plays in this structure the same part as does the central XO_4 tetrahedron in Keggin's structure for the 12-poly-acids.

⁴³ A. J. Bradley and J. W. Illingworth, *ibid.*, 1936, A, 157, 113.

⁴⁴ J. W. Illingworth and J. F. Keggin, *J. Chem. Soc.*, 1935, 575; J. A. Santos, *Proc. Roy. Soc.*, 1935, A, 150, 309; O. Kraus, *Z. Krist.*, 1935, 91, 402; 1936, 93, 379.

⁴⁵ Cf. Pauling, ref. 40. This hypothesis has, in fact, been verified for the 18-tungsto 2-phosphate (B. Dawson, unpublished).

⁴⁶ J. S. Anderson, *Nature*, 1937, 140, 850.

It is noteworthy that the elements which can serve as central atoms in the 6-poly-acids are just those which exhibit the co-ordination number 6 in their oxy-acids ($\text{H}_7[\text{IO}_6]$, $\text{H}_6[\text{TeO}_6]$) or their hydrated oxides (FeO.OH , Al(OH)_3).

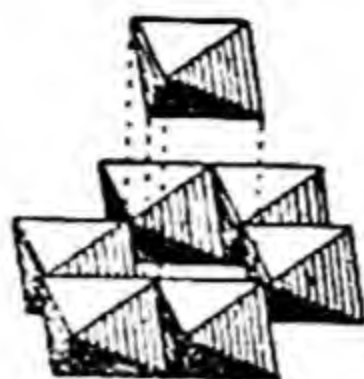
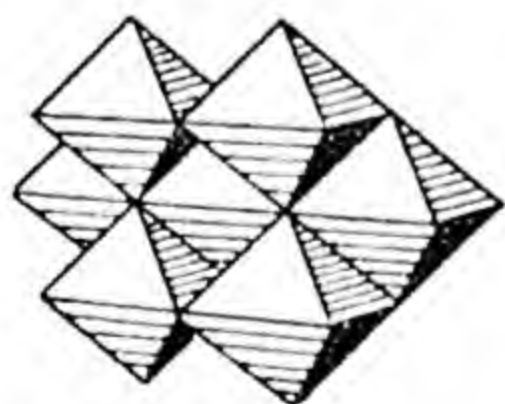


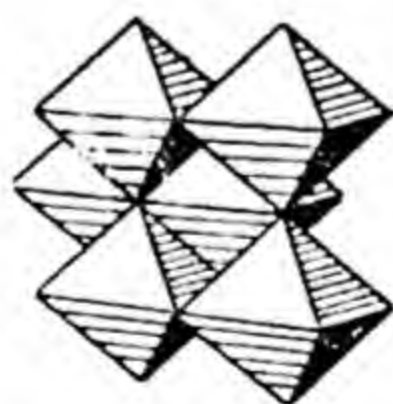
FIG. 35.—The structure of the $[\text{TeMo}_6\text{O}_{24}]^{6-}$ ion.

The structure represented in Fig. 35, proposed for the 6-poly-acids on stereochemical grounds, has been found by Evans⁴⁷ to represent correctly the anion of potassium and ammonium molybdotellurate.

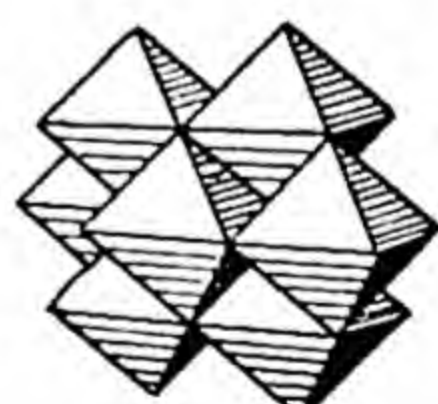
Since the paramolybdates have been shown to have the formula $\text{R}_6[\text{Mo}_7\text{O}_{24}]$, it might be supposed that they could be regarded essentially as 6-poly-acids, but with molybdenum serving also as the central atom of the complex, $\text{R}_6[\text{Mo.Mo}_6\text{O}_{24}]$. Lindqvist⁴⁸ finds that whilst the $[\text{Mo}_7\text{O}_{24}]$ anion is, indeed, based on the same principles as the structure discussed, its structure is that shown in Fig. 36a, differing from the other in the manner of sharing of two octahedron edges. In the light of what has been said above about ageing processes in solutions, it may perhaps be significant that in the 6-molybdotellurates and the paramolybdates there are found two variants of a 6-poly-acid structure, convertible one into the other by the hydrolytic opening and reformation of a pair of oxygen bridges.



(a)



(b)



(c)

FIG. 36.

The octomolybdates contain a complex anion of analogous structure⁴⁹ (Fig. 36c). The configuration of this anion, however, is such

⁴⁷ *J. Amer. Chem. Soc.*, 1948, 70, 1291.

⁴⁸ I. Lindqvist, *Arkiv f. Kemi*, 1950, 2, 325.

⁴⁹ I. Lindqvist, *Arkiv f. Kemi*, 1950, 2, 349.

that it cannot be formed by the direct condensation of an MoO_4^{2-} group with the paramolybdate ion. These do not, therefore, exactly represent successive stages in the condensation. It is highly suggestive, however, that both species could be formed by condensation processes from the same hexamolybdate unit (Fig. 36b); even though this has not yet been met with in a crystalline salt, the evidence for its existence in solution is strong.

Jahr⁵⁰ has pointed out that the compact structure of Fig. 35, now proved experimentally, could be incorporated in the 12-poly-acid also, if the four M_3O_{13} groups may be slightly rearranged, to share octohedron edges instead of corners. How far this modification would be in accord with Keggin's X-ray data is not clear. If it were verified it would hold the attractive implication that the same unit which exists in acid solutions (if, as is plausible, the ion written formally as $[\text{HM}_6\text{O}_{21}]^{5-}$ can legitimately be written with water of constitution, as $[\text{HM}_6\text{O}_{18}(\text{OH})_6]^{5-}$) appears as a structural unit in both the 6-poly-acids and the 12-poly-acids.

The problem of the basicity of the poly-acids may well be bound up with the possibility of opening up oxygen bridges by hydration. As it stands, the Keggin cage model rigidly imposes on the 12-poly-acids the basicity of the central acid. This leaves unexplained the high basicities reported for certain silver, mercury, guanidinium and other salts. If these were basic salts, it would be surprising that their composition should so often agree with the basicities required by Rosenheim's theory. The ferric 12-tungstosilicate, $\text{Fe}_5\text{H}[\text{SiW}_{12}\text{O}_{40}]_2 \cdot 52\text{H}_2\text{O}$, which has been very well characterized,⁵¹ can hardly be formulated in any other way than with an 8-basic anion. This basicity can be attained only if some of the water molecules are constitutional—e.g. $\text{Fe}_5\text{H}[\text{SiW}_{12}\text{O}_{40}(\text{OH})_4]_2 \cdot 48\text{H}_2\text{O}$. It has also been observed that 12-tungstophosphoric acid displays two equivalence points, corresponding to the addition of 3 and 7 equivalents of alkali respectively. In this case it is not clear whether the potential basicity is really four units higher than that given by the Keggin formula, or whether the second end point represents the completion of a degradation reaction.^{30, 52}

The Polyphosphoric Acids.—In the systems just discussed, the process of formation of condensed acids leads, in every case, to the formation of discrete anions. By contrast, the silicates are based largely, though not exclusively, upon the infinite condensation of $[\text{SiO}_4]$ groups, as will be discussed in a later section. Their

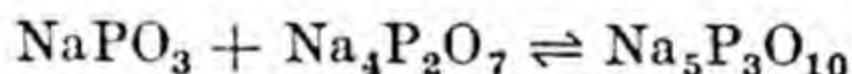
⁵⁰ *Naturwiss.*, 1941, 29, 528; O'Daniell, *Z. Krist.*, 1942, 104, 225.

⁵¹ O. Kraus, *Naturwiss.*, 1939, 27, 740.

⁵² Nikitina, *J. Gen. Chem. Russ.*, 1940, 10, 779, claims to have prepared $\text{Na}_7[\text{PW}_{12}\text{O}_{42}] \cdot aq$.

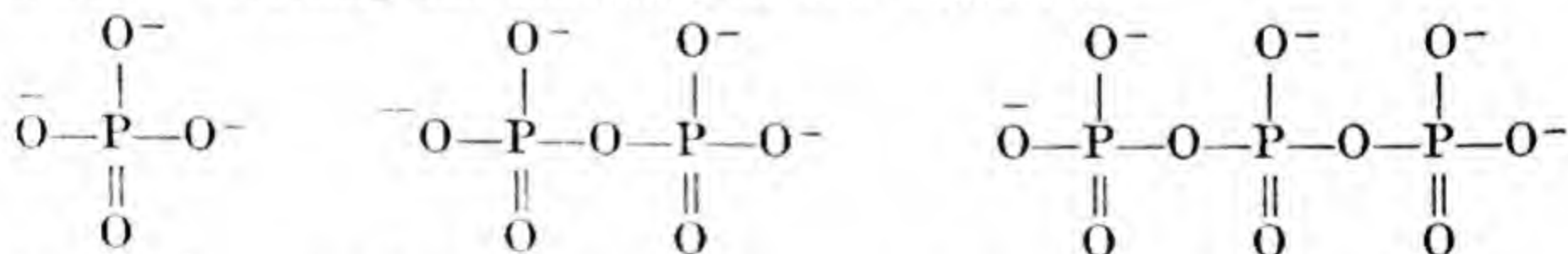
chemistry is concerned with the solid state, and not with equilibria in aqueous solution. The oxy-acids of the Group V elements stand between these two classes of poly-acid systems, and work of the last few years has shown that the phosphoric acids, and probably the arsenic acids also, represent an intermediate stage, between the two extreme classes.^{52a}

The existence of three stages in the hydration of phosphorus pentoxide, represented by the orthophosphates, pyrophosphates and metaphosphates respectively, was first recognized and correctly interpreted by Thomas Graham, in 1833.⁵³ Graham showed that by dehydrating disodium hydrogen phosphate and sodium dihydrogen phosphate, the pyrophosphate and the metaphosphate respectively were obtained. Fleitmann and Henneberg,⁵⁴ and subsequently other workers also, claimed that when mixtures of sodium metaphosphate and pyrophosphate were heated they formed the sodium salts of more highly condensed polyphosphoric acids—*e.g.* $\text{Na}_5\text{P}_3\text{O}_{10}$, $\text{Na}_6\text{P}_4\text{O}_{13}$ and $\text{Na}_{12}\text{P}_{10}\text{O}_{31}$. The existence of these compounds was in dispute for a long time, but it now seems to be firmly established^{55, 56} that the only compound found by thermal analysis in the system $\text{NaPO}_3 + \text{Na}_4\text{P}_2\text{O}_7$ is the triphosphate. This is formed⁵⁷ with remarkable rapidity at 600° by the solid phase reaction



but decomposes peritectically at about 620° .

The conversion of these phosphoric acids one into another involves irreversible high temperature processes, and not the reversible acid-base relationships discussed in the last section. Structurally, however, the first stages of condensation take place quite normally, by the linkage of co-ordination polyhedra through shared oxygen atoms. Writing the formulæ of the anions as



it may be seen that they are built up on the principle already mentioned by sharing oxygen atoms between tetrahedral PO_4^{3-} groups.

^{52a} B. Topley, *Chem. Soc. Quart. Rev.*, 1949, 3, 345.

⁵³ *Phil. Trans.*, 1833, 123, 253.

⁵⁴ *Annalen*, 1848, 65, 324.

⁵⁵ K. R. Andress and K. Wüst, *Z. anorg. Chem.*, 1938, 237, 113; 1939, 241, 196.

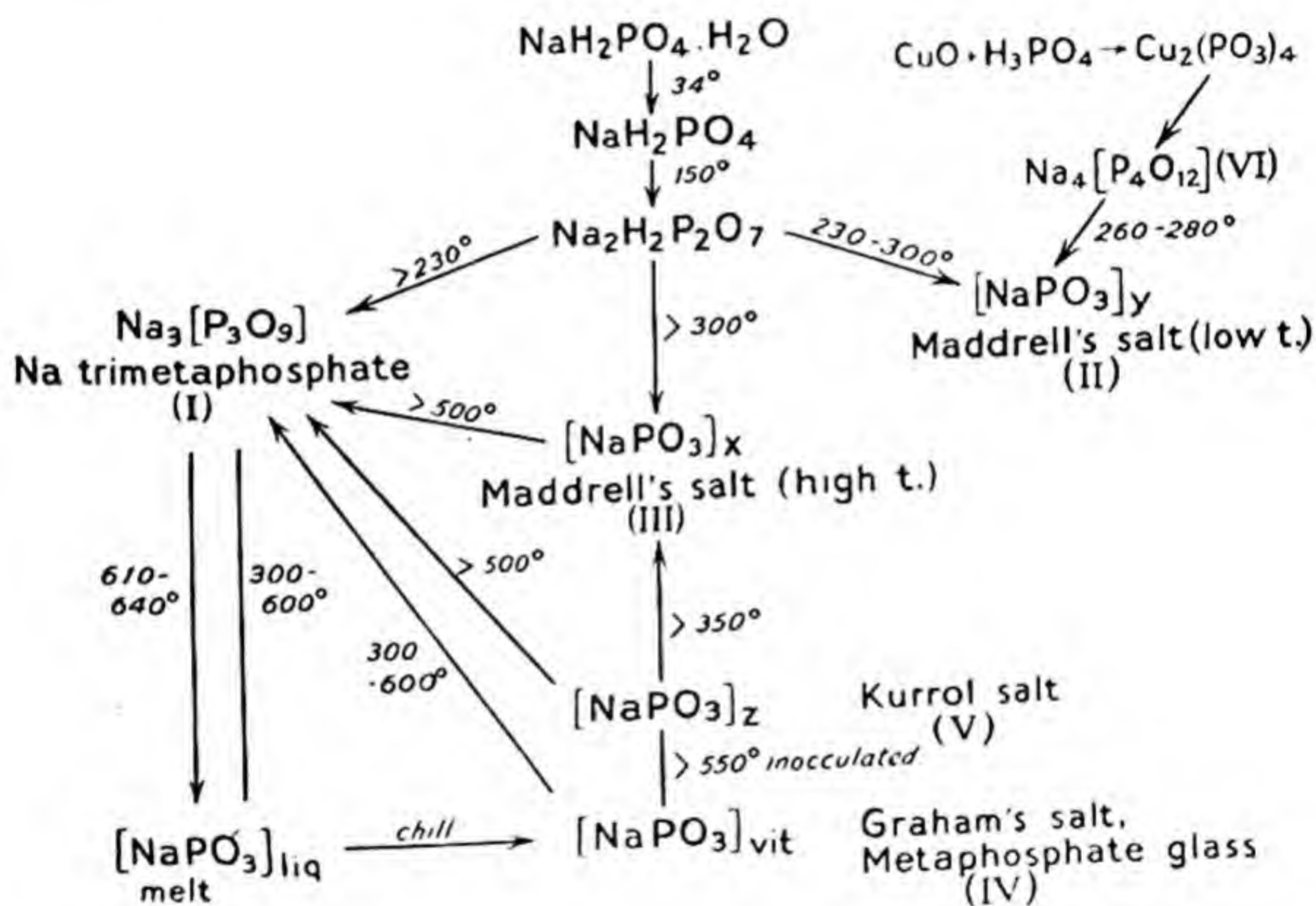
⁵⁶ E. P. Partridge, V. Hicks and G. W. Smith, *J. Amer. Chem. Soc.*, 1941, 63, 454.

⁵⁷ T. Schwarz, *Z. anorg. Chem.*, 1895, 9, 249; H. Huber, *ibid.*, 1936, 230, 133.

In each case it has been observed that one hydrogen atom per atom of phosphorus behaves as a strongly acidic hydrogen, the remaining hydrogen atoms being relatively weakly dissociated. This property shows up clearly in potentiometric titrations and through the formation of acid pyrophosphates and triphosphates, such as $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$, $\text{Na}_3\text{H}_2\text{P}_3\text{O}_{10}$.

The metaphosphates cannot be immediately fitted into this scheme of condensation processes. They present a picture of such complexity that only during the last few years has it been at all possible to interpret their formation and structure. Whereas the

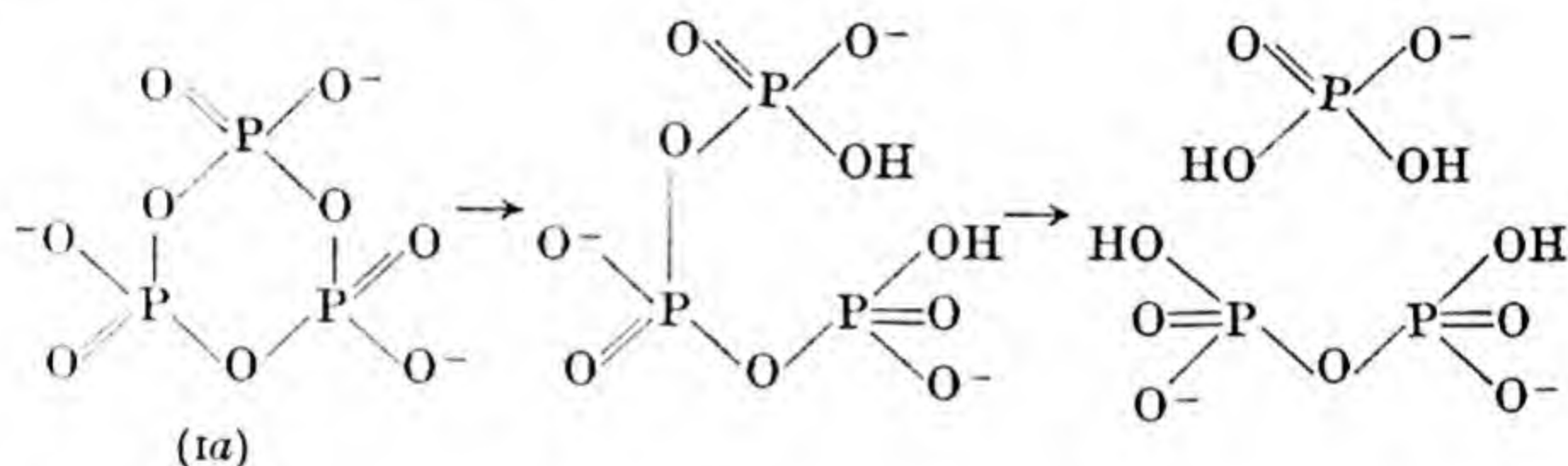
Table 5



ortho-, pyro- and triphosphoric acids are clearly defined chemical species, the physical properties and chemical reactions of metaphosphoric acid and its salts—and therefore their molecular complexity also—are highly dependent upon the nature of the starting material, the mode of preparation of each specimen and its subsequent heat treatment, and point to the existence of at least several compounds with the same empirical formula $(\text{HPO}_3)_n$. The relations between the principal species of metaphosphates, as they emerge from the work of Partridge, Hicks and Smith,⁵⁶ Thilo and Raetz⁵⁸ and earlier workers, is summarized by Table 5 above.

⁵⁸ *Z. anorg. Chem.*, 1949, 258, 33.

The dehydration of sodium dihydrogen phosphate leads to the simultaneous formation of two products, in varying amounts, with the same empirical formula NaPO_3 . These are a soluble salt (I), and an insoluble compound, still the least known of the metaphosphate species, named Maddrell's salt, after its discoverer.⁵⁹ It has since been shown that there are two modifications of Maddrell's salt, (II) and (III), formed at low temperatures and high temperatures respectively. Both are thermodynamically unstable with respect to the soluble salt (I), which is, indeed, the end product of annealing of any of the forms of sodium metaphosphate at 550–600°. This salt (I) is shown beyond doubt to be sodium trimetaphosphate, $\text{Na}_3[\text{P}_3\text{O}_9]$, by cryoscopic evidence,⁶⁰ by measurements of ionic weight⁶¹ and by its hydrolysis, first to $\text{Na}_3\text{H}_2\text{P}_3\text{O}_{10}$ and an equimolecular mixture of orthophosphate and pyrophosphate—



The cyclic structure (Ia) for the anion accords with the fact that fresh solutions of the free acid give titration curves indistinguishable from those of a strong monobasic acid: all the hydrogen atoms are equivalent and strongly acidic. Such a cyclic $[\text{P}_3\text{O}_9]^{3-}$ anion has, in fact, been identified in the crystal structure of strychnine metaphosphate. All the salts of trimetaphosphoric acid (including those of Ca, Sr, Ba, Ag and Pb) are soluble in water.

There is a second crystalline, soluble class of metaphosphates, prepared by the action of phosphoric acid on the oxides of heavy metals⁶² and formerly called 'dimetaphosphates'. They are actually tetrametaphosphates (VI), as has been shown by cryoscopic measurements,^{60, 63} and contain the cyclic anion (VIa); this has been found in the crystal structure of the aluminium salt, $\text{Al}_4[\text{P}_4\text{O}_{12}]_3$. Sodium tetrametaphosphate hydrolyses to a mixture of pyrophos-

⁵⁹ Liebig's *Ann.*, 1847, 61, 53.

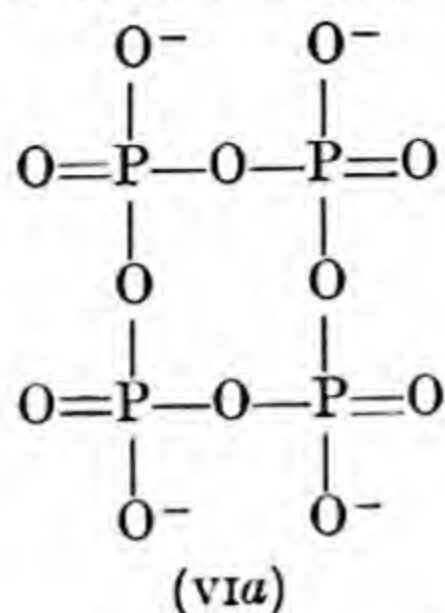
⁶⁰ P. Nylen, *Z. anorg. Chem.*, 1936, 229, 30.

⁶¹ W. Teichert and K. Rinman, *Acta Chem. Scand.*, 1948, 2, 225.

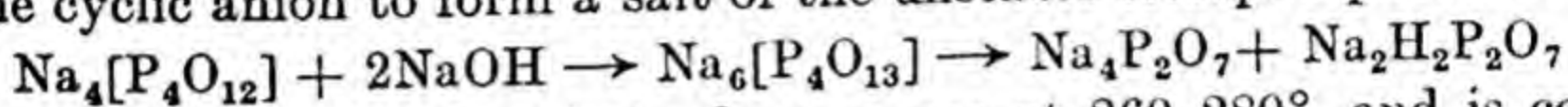
⁶² Fleitmann, *Pogg. Ann.*, 1849, 78, 233, 338; Warschauer, *Z. anorg. Chem.*, 1903, 36, 137.

⁶³ Bonnemant-Bemia, *Ann. Chim.*, 1941, 15, 457.

phate and orthophosphate, but according to Thilo and Raetz,⁶⁴ careful hydrolysis with the theoretical quantity of alkali first opens



the cyclic anion to form a salt of the unstable tetraphosphoric acid.



Sodium tetrametaphosphate decomposes at 260–280°, and is converted directly to Maddrell's salt.

Graham's Salt.—All the forms of sodium metaphosphate melt at 610–620°, forming a viscous fluid. This has strong solvent properties for metallic oxides, which it dissolves in the form of their orthophosphates. The crystallizing propensities of the melt are very poor, and when it is cooled rapidly it solidifies to a vitreous substance known as Graham's salt. As Graham noticed, this is soluble in water and its solution is not rapidly hydrolysed at the ordinary temperature. The solution has the property of forming complex compounds (of as yet uncertain constitution) with the cations of calcium and other bivalent metals, and of inhibiting the precipitation of carbonates. For this reason, Graham's salt has found extensive application in the treatment of boiler feed water, and much of the scientific interest recently evinced in the chemistry of metaphosphoric acid can be traced to the technological interest in Graham's salt.

On rather inadequate evidence, Fleitmann (1849) concluded that Graham's salt is sodium hexametaphosphate, $\text{Na}_6[\text{P}_6\text{O}_{18}]$, and this name has been perpetuated in common usage. However, the supposed ethyl ester of hexametaphosphoric acid, as described by Pascal (1923), has properties (insolubility in ether, partial solubility in chloroform) which suggest that a mixture of high-molecular metaphosphoric esters must have been obtained. Definite evidence for the constitution of Graham's salt was first forthcoming when Lamm and Malmgren,⁶⁵ by means of sedimentation measurements, and Karbe and Jander,⁶⁶ from dialysis and diffusion measurements, showed it to be a high polymer of sodium metaphosphate, $[\text{NaPO}_3]_n$.

⁶⁴ *Z. anorg. Chem.*, 1950, 260, 255.

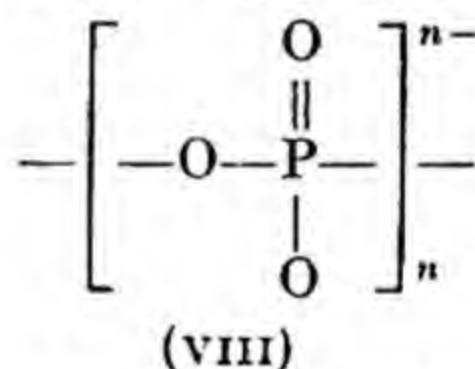
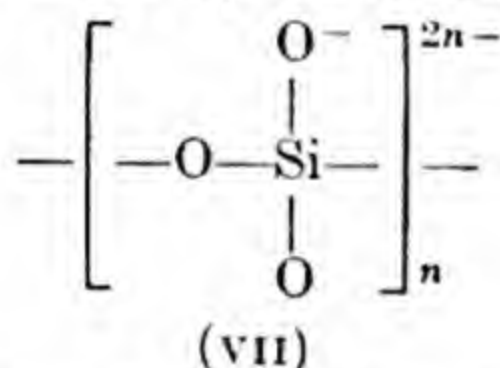
⁶⁵ *Z. anorg. Chem.*, 1940, 245, 103.

⁶⁶ *Kolloid Beih.*, 1942, 54, 1.

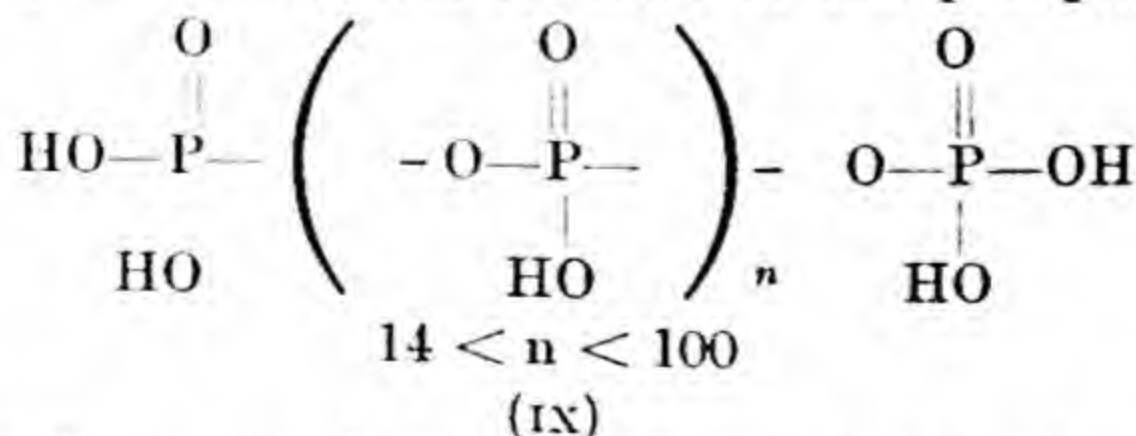
where—according to Karbe and Jander— n varies in the range 34–90. The degree of polymerization is uncertain, but undoubtedly increases with the temperature from which the melt is quenched—*e.g.* from $n = 16$ in material quenched from 650° to $n = 35$ when quenched from 900° .⁶¹

When it is annealed above 550° , and especially if it is inoculated with the end product, Graham's salt is partly converted into a substance of fibrous texture, which resembles asbestos and gives a fibre X-ray pattern. It is known after its discoverer as Kurrol salt.⁶⁷ This is insoluble in water, but swells to a gel, especially if univalent or bivalent ions are present in the solution. The relationship of Kurrol salt to Graham's salt and Maddrell's salt has not yet been fully explained. Its mode of formation suggests that it may be essentially an oriented, crystalline form of Graham's salt, not necessarily of very different complexity. Maddrell's salt is more insoluble than Kurrol salt and it may, perhaps, be concluded that it represents yet a further stage in the polymerization process.

The morphological resemblance between Kurrol salt and the typical fibrous metasilicates (*q.v.*) suggests that they are of similar structure. Just as the metasilicates are based upon long-chain anions (VII), so in the high-molecular metaphosphates the anion may be built up from many units of (VIII). The differences in



solubility and fusibility would be explained in part by the smaller ionic charge per unit of structure in the metaphosphates. Whereas, however, the metasilicate chains are, in effect, of infinite length, existing only in the structure of crystalline substances, it is evident that in Graham's salt the metaphosphate chain may involve only 16–40 or 100 units. The two ends of the chain must accordingly be terminated by suitable groups—*e.g.* by --OH . We therefore arrive at (IX) as the typical formula of the phosphoric acids of



⁶⁷ G. Tammann, *J. prakt. Chem.*, 1892, [ii], 45, 417.

Graham's salt and Kurrol salt. This formula is, strictly, that of a *polyphosphoric acid*, of the same series as $H_4P_2O_7$, $H_5P_3O_{10}$, etc., rather than a polymer of metaphosphoric acid.

If it is valid to assume that only one hydrogen atom per atom of phosphorus behaves as belonging to a strong acid, it may be seen that the end groups introduce two weak acid groups into the molecule, as compared with $n + 2$ strong acid groups. On this basis, the proportion of weak acid groups, as determined by accurate potentiometric titration, should afford a measure of the chain length. Such measurements have been carried out,⁶⁸ and when re-interpreted in the light of current views on the high-molecular metaphosphates they lead to chain lengths of 70–100 for Graham's salt—*i.e.* of the same order as is derived from other data.

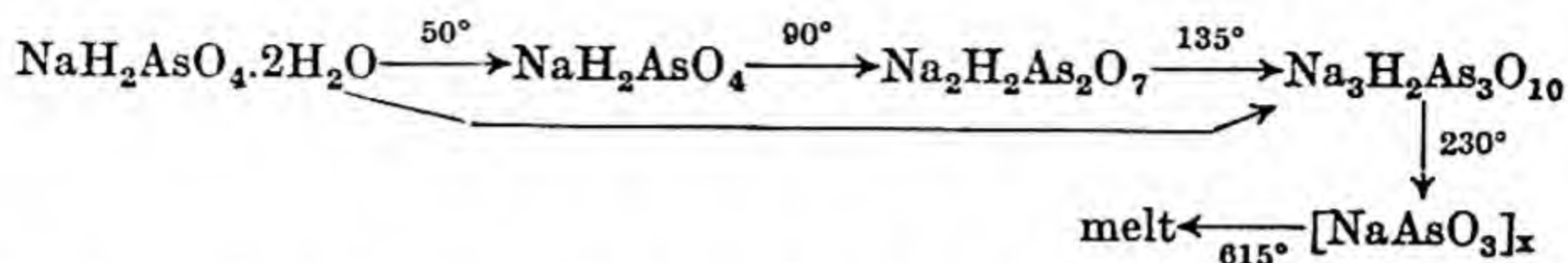
These views account for the properties of the metaphosphates in solution. The processes occurring at high temperatures and in the melt need some consideration, however, as it is necessary to specify the nature of the chain-terminating groups if the linear polymer formulæ are to be applied to the solid Graham's and Kurrol salts. The key to this problem is furnished by the observation⁶⁹ that the metaphosphate melt is never rigorously anhydrous. Even at 700° it retains sufficient water—which is unquestionably constitutional, and not free H_2O —to provide terminal groups for the polyphosphate chains. The process of chain growth at higher temperatures is primarily the result of progressive expulsion of water. All other forms are ultimately converted into trimetaphosphate on annealing, not only because that form is the thermodynamically stable species, but because it is the ultimate product of dehydration. The crystallization of $Na_3[P_3O_9]$ is attended with loss of water, and all the reactions leading to this step are effectively irreversible accordingly. The evolution and re-sorption of water within the solid phase or the melt confers a certain mobility on the system, and chain rupture can produce either the stable cyclic $[P_3O_9]^{3-}$ group or, by recombination of polymer fragments, a lengthening of the chain. In this way the trimetaphosphate and Maddrell's salt could be produced concurrently, as alternative products, during the annealing of Kurrol salt or of tetrametaphosphate.

Polymeta-arsenates.—The formation of poly-acids by arsenic has received but little study as yet, in comparison with the polymetaphosphates. It is, however, clear that there is a great difference in stability and reactivity between the phosphate and arsenate systems.

⁶⁸ Rudy and Schloesser, *Ber.*, 1940, 73, 484; Samuelson, *Svensk. Kem. Tidskr.*, 1944, 56, 343.

⁶⁹ Huber and Klumpner, *Z. anorg. Chem.*, 1943, 251, 213.

The dehydration of sodium dihydrogen arsenate gives rise successively to the simpler polyarsenates and to polymetarsenate, but distinct forms of the metarsenate have not been characterized.



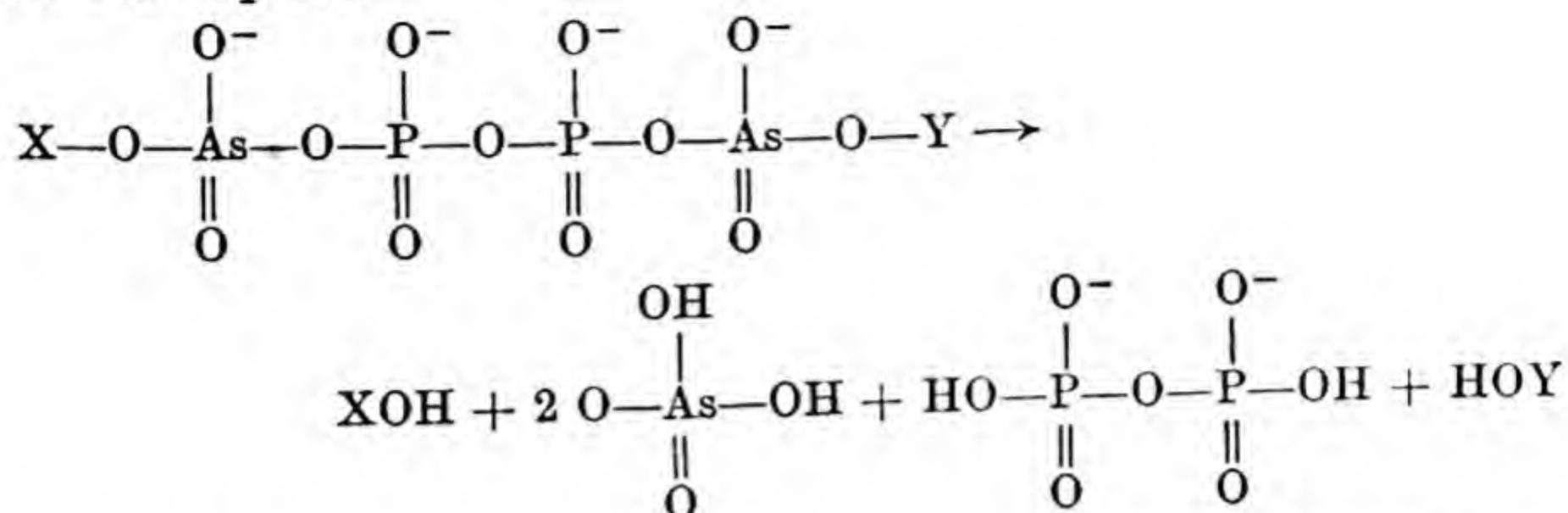
The products of dehydration react with water vapour, and successive stages in rehydration can be identified. When the metarsenate is treated with an ethereal solution of the theoretical amount of water, it reforms $\text{Na}_3\text{H}_2\text{As}_3\text{O}_{10}$.⁷⁰ However, the act of dissolution of any of the polyarsenates in water produces rapid and complete hydrolysis. It is evident that the As—O—As bridge in the polyarsenic acids is severed much more readily than the corresponding linkage in the polyphosphoric acids. Thilo has suggested that this is because arsenic can increase its co-ordination number from 4 to 6. In keeping with this view is the extremely hygroscopic nature of arsenic acid, which exists at the ordinary temperature as $\text{H}_3\text{AsO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$, and, below -30° , as $\text{H}_3\text{AsO}_4 \cdot 2\text{H}_2\text{O}$, or $\text{H}[\text{As}(\text{OH})_6]$.

The ease of hydrolysis of polyarsenate chains has been utilized by Thilo and Plaetschke⁷¹ to study the constitution of the linear polyphosphates, since it has been shown that mixed melts of NaH_2PO_4 and NaH_2AsO_4 , containing not less than 20 mol. per cent of arsenate, give homogeneous products, $[\text{Na}(\text{As},\text{P})\text{O}_3]_x$, in the form of fine needles. The X-ray diffraction patterns and the densities vary with composition in such a way as to link these substances with Maddrell's salt rather than Kurrol salt, through the progressive replacement of phosphorus by arsenic. Whereas Maddrell's salt is insoluble, the ease of dissolution in cold water increases progressively as phosphorus is replaced by arsenic. Dissolution is rapidly followed by hydrolysis of the As—O—As and As—O—P linkages, so that although a fresh solution gives, with silver nitrate, a white precipitate of $[\text{Ag}(\text{As},\text{P})\text{O}_3]_x$, this rapidly changes colour and is converted to brown Ag_3AsO_4 and yellow Ag_3PO_4 . There is some evidence that, in the annealed crystals, the AsO_4 tetrahedra are built into the anionic chains in a regular fashion. Thus from a preparation with As : P = 1 : 2, much of the phosphorus is recoverable as pyrophosphate. Taken in conjunction with the known behaviour of the linear polyphosphates, this would imply that the

⁷⁰ E. Thilo and I. Plaetschke, *Z. anorg. Chem.*, 1950, **260**, 315.

⁷¹ *Z. anorg. Chem.*, 1950, **260**, 297.

linear poly-anion had the phosphorus atoms adjacent to one another, in the sequence



There is as yet no evidence of the formation of true metarsenates—*e.g.* compounds such as $\text{Na}_3[\text{As}_3\text{O}_9]$. When mixtures containing $\text{P} : \text{As} > 4 : 1$ are annealed, $\text{Na}_3[\text{P}_3\text{O}_9]$ is formed, but it incorporates no metarsenate in its structure.

THE SILICATES

The complexity of the naturally occurring silicate minerals presented a problem which proved quite insoluble by chemical methods alone. The application of X-ray crystallographic methods, however, has served to reveal certain broad principles upon which the structures of the silicates are based.

Amongst the obstacles to the study of the silicates has been, in the past, the difficulty of assigning to the compounds correct and significant molecular formulæ. This difficulty arises from several causes. In the first place, since the analytical data for such complex materials may be compatible with several different molecular formulæ, the uncertainty which is inherent as to the homogeneity and reproducibility of material of natural origin limits the possibility of decisive formulation on analytical grounds alone. Secondly, as is well known, the question is complicated by the isomorphous replacement of one element by another in the simple sense of Mitscherlich's law. Thus, magnesium, calcium, ferrous iron and other bivalent metals may replace one another mutually to a greater or lesser extent, as also may Al^{3+} and Fe^{3+} , or OH' and F' . In such replacements, the number of ions of each valency type remains unchanged, although some difficulty may arise in the correct assignment of elements of variable valency. There is, however, a second kind of isomorphous replacement which is of frequent occurrence and which may be far-reaching in extent, thereby altering the whole apparent formulation of the compound. This represents a principle of great importance in the building up of

silicate structures. As is dealt with more fully below, the similarity in ionic radius between, *e.g.*, aluminium and silicon leads to the possibility of the replacement of silicon in the anion atom for atom by aluminium. The valency of the anion is thereby raised by one unit, and this increase must be compensated by a corresponding increase of the total cationic charge. This can be brought about either by introducing additional cations, or by some such process as the corresponding isomorphous replacement of sodium by calcium. In such cases, the assignment of a formula from analytical data would require a knowledge of the distribution of certain elements between anionic and cationic functions.

It is not surprising, therefore, to find that the X-ray investigations have in some cases modified accepted formulæ. They have also provided a more precise significance for silicate formulæ, as representing, not the nature of discrete molecules, but rather the atomic composition of those simplest structural units out of which the whole three-dimensional pattern of the silicate crystal is built.

Structural Principles of the Silicates.⁷²

The structure of the silicates can be regarded as based in all cases on the formation of co-ordination lattices of large anions about small cations. Silicon may be regarded as being present in the form of a Si^{4+} ion; the anions are, in general, O^{2-} ions. These, being of much greater size than any of the positive ions concerned (Table 6), play the chief role in determining the dimensions and general skeleton of the whole structure. According to W. L. Bragg, the distance between oxygen atoms of any one structural group is always 2.6–2.8 Å; that between adjacent oxygen atoms of different groups is about the same. Hence, in the case of the simpler silicates, the whole can be looked on as a close-packed assembly of oxygen ions, with the relatively small silicon and other cations so fitted into the interstices that each is co-ordinated (in the crystallographic sense) with the appropriate number of oxygen ions. The co-ordination number of a cation in such a structure is governed solely by the relative radii of the central cation and the surrounding anions, according to the relationship worked out by V. M. Goldschmidt and briefly considered earlier in this chapter⁷³ (Tables 3 and 4, above).

From a comparison of Table 6 with Tables 3 and 4, it may be seen that silicon must have the co-ordination number four, and so

⁷² See W. L. Bragg, *Trans. Faraday Soc.*, 1929, 25, 291; *The Structure of the Silicates*, Julius Springer; *Roy. Inst. Proc.*, 1927, 121; and especially *Atomic Structure of Minerals*, Oxford, 1937.

⁷³ *Ber.*, 1927, 60, 1263.

will invariably be found in the centre of a tetrahedral arrangement of oxygen atoms. Magnesium, similarly, will invariably be octo-

Table 6

Radii of Ions Common in Silicate Minerals

Be ²⁺	0.39 Å	Ca ²⁺	0.98 Å
Si ⁴⁺	0.50	Na ⁺	0.98
Al ³⁺	0.55	K ⁺	1.33
Fe ³⁺	0.67	O ²⁻	1.40
Mg ²⁺	0.71	OH ⁻	1.40
Fe ²⁺	0.83	F ⁻	1.33

hedrally co-ordinated. The aluminium ion, however, is of such a radius that it may be co-ordinated either with four or six oxygen atoms. It is thus at once clear that aluminium may play the two-fold role of isomorphous replacement of silicon inside tetrahedral units, and of magnesium inside octohedra.

From the chemical point of view, the anion of the whole lattice will be an assembly of oxygen ions with the silicon ions (and, in the aluminosilicates, the aluminium ions) co-ordinated between them. It will be characterized, and its formula determined, by the number of oxygen atoms within the unit of pattern; its basicity is given by the uncompensated ionic charge. The oxygen ions may be common to several co-ordination polyhedra, so that in the formulation of the silicates the following possible types arise:

(A) Silicates with *discrete anions*.

(i) Orthosilicates. SiO_4^{4-}

(ii) More complex units— $\text{Si}_2\text{O}_7^{6-}$, $\text{Si}_3\text{O}_9^{6-}$, $\text{Si}_6\text{O}_{18}^{12-}$.

(B) Silicates with *extended anions*.

(i) Chains of linked SiO_4 tetrahedra. SiO_3^{2-} , $\text{Si}_4\text{O}_{11}^{6-}$.

(ii) Sheets, made by cross-linking of chains. $\text{Si}_2\text{O}_5^{2-}$.

(C) *Three-dimensional networks*, formed by cross-linking of superimposed sheets.

(A, i) *Orthosilicates*.—The structure of the orthosilicates is, as indicated, built up from independent SiO_4^{4-} tetrahedra (Fig. 37). The oxygen atoms of these compact tetrahedra are co-ordinated to the metallic cations, each oxygen atom being then common to several cation polyhedra. The possibility of effecting this in different ways makes possible the existence of several distinct orthosilicate structures.

Thus, in olivine, $(\text{Mg,Fe})_2\text{SiO}_4$, magnesium ions are so packed between the SiO_4 tetrahedra that each magnesium ion is between six oxygen atoms. Each oxygen is then linked directly to one silicon atom and co-ordinated jointly to three magnesium atoms.

Pauling ⁷⁴ has laid down the rule, governing the formation of such co-ordination lattices, that in stable structures the charge on each anion is equal and opposite to the sum of the electrostatic valency bonds reaching it from the cations of the polyhedra to which it is common. Thus, the magnesium ion (charge + 2 units), being co-ordinated in an octohedron, directs an electrostatic valency bond

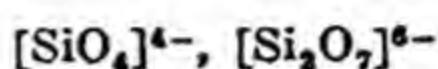
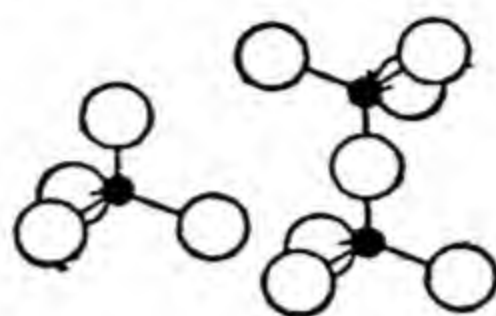


FIG. 37.—Discrete silicate anions—e.g. the orthosilicate anion.

of strength $1/3$ to each oxygen ion. In the olivine structure, therefore, the nett electrovalencies reaching each oxygen ion are

$$\left. \begin{array}{l} \text{from three } \text{Mg}^{2+} \text{ ions, } 3 \times 1/3 = +1 \text{ unit} \\ \text{from the central } \text{Si}^{4+} \text{ ion of each tetrahedron} \quad \quad \quad +1 \text{ unit} \end{array} \right\} = +2 \text{ units in all,}$$

balancing the intrinsic charge -2 units on each oxygen ion.

Various other silicate minerals are based upon the olivine structure. Thus, the chondrodite group,⁷⁵ $\text{Mg}(\text{OH}, \text{F})_2 \cdot n\text{Mg}_2\text{SiO}_4$, where $n = 1, 2, 3$ or 4 , consists of sheets of the olivine structure interleaved with layers of OH ions or F ions (which are nearly identical, in size). The OH and F ions are not part of silicon tetrahedra, but are so situated that, together with the oxygens of the SiO_4 groups, they go to make up octohedra surrounding the magnesium ions. The structures of the various minerals of this group are all of this type, being derived from one another by variation in the relative positions of the olivine and OH sheets.

In phenacite, Be_2SiO_4 , and willemite, Zn_2SiO_4 , an entirely different structure obtains, since the metal ions must here be tetrahedrally co-ordinated. Each oxygen atom is then common to one silicon tetrahedron and two MO_4 tetrahedra. As may readily be seen, the Pauling rule is again exemplified.

(A, ii) Introduction of larger discrete anions gives more complex structures. Of these, the $(\text{Si}_6\text{O}_{18})^{12-}$ unit, found for example in beryl, $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$, is particularly important. Just as all the more complex structures are based on SiO_4 tetrahedra sharing corners, so the Si_6O_{18} unit, consisting of six SiO_4 tetrahedra linked in a ring (Fig. 38), enters into the structure of the more highly condensed

⁷⁴ *J. Amer. Chem. Soc.*, 1929, 51, 1010.

⁷⁵ See W. L. Bragg, *Trans. Faraday Soc.*, 1929, 25, 291.

sheet-like and three-dimensional silicate anions. In beryl, such rings are joined together by the co-ordination of their oxygen atoms to the metallic cations. The Si_6O_{18} groups in different layers are so disposed that wide channels, roughly large enough to accommodate an oxygen atom, are formed down the centre of superimposed Si_6O_{18} hexagons. It is interesting to correlate this open structure, with its potential permeability to small gas molecules, with the well-known occlusion of helium by beryl.

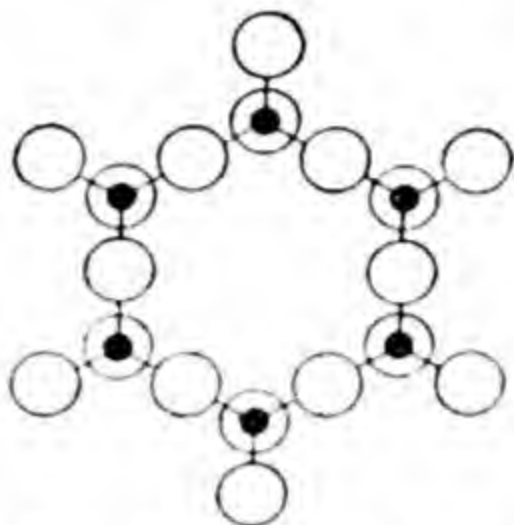


FIG. 38.—The $(\text{Si}_6\text{O}_{18})^{12-}$ group structure found in beryl.

(B, i) *Metasilicates*.—The metasilicate anion, SiO_3^{2-} , is formed by the linking up of SiO_4 tetrahedra in an endless chain (Fig. 39). Two oxygen atoms of each tetrahedral group are then unshared, and two are shared with neighbouring silicon atoms. The resulting chain can be infinite in length, and extends, in fact, throughout the crystal. Such a macro-anion is found in diopside, $\text{MgCa}(\text{SiO}_3)_2$.

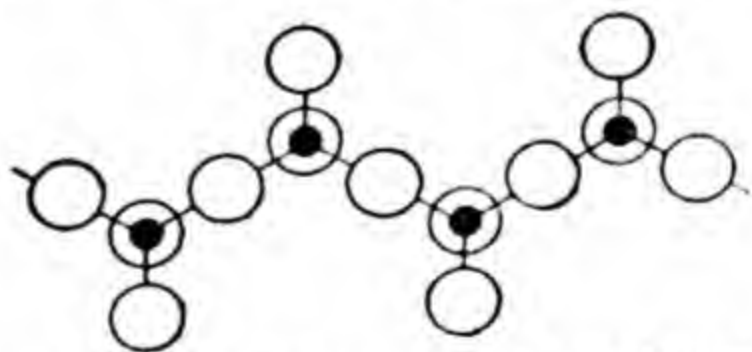


FIG. 39.—Chain-like metasilicate $(\text{SiO}_3)^{2-}$ group.

The amphibole mineral tremolite, formerly formulated as $\text{H}_2\text{Ca}_2\text{Mg}_5(\text{SiO}_3)_8$, has a crystal structure very closely related to that of diopside, the principal difference being that the length of the b axis of the crystal is doubled. Warren has shown that tremolite should be correctly formulated as $(\text{HO})_2\text{Ca}_2\text{Mg}_5(\text{Si}_4\text{O}_{11})_2$, with a $\text{Si}_4\text{O}_{11}^{6-}$ anion. This is formed by cross-linking two diopside chains, by a further sharing of tetrahedron corners (Fig. 40).

In these metasilicates, the important relationship between crystal structure and physical properties is clearly to be seen. The chains are in all cases arranged parallel to the c axis of the crystal, and are bound laterally to one another by co-ordination of their oxygen

atoms to calcium or magnesium ions. The resulting structure is mechanically weak in directions parallel to the length of the chains, since fracture in this direction is across the metal-oxygen links only. In a direction at right angles to the chains, however, fracture would involve a breakage of the chain itself with the severance of the strong silicon-oxygen bonds. In accordance with this conception, cleavage of the crystals is highly developed parallel to the *c* axis, and the minerals frequently exhibit a fibrous structure—notably in asbestos, a form of amphibole. In principle, there is, of course, no difference between the kind of electrostatic bond between silicon and oxygen, and that between the metallic cations and oxygen. Since silicon, with a co-ordination number four, is quadrivalent, each Si—O bond is of strength unity (*cf.* above, p. 238). The Ca—O or Mg—O bonds, for example, are only each

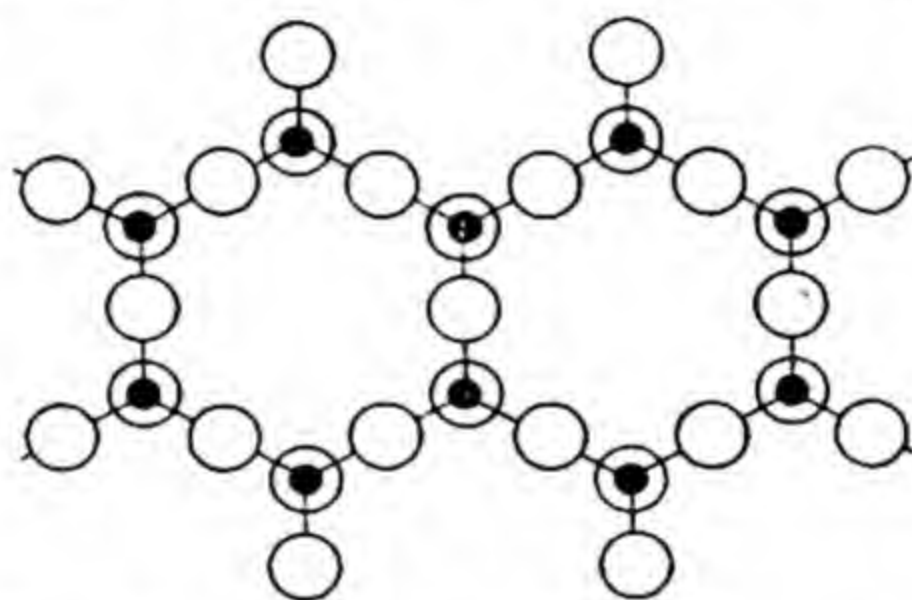


FIG. 40.—Cross-linked $(\text{Si}_4\text{O}_{11})^{6-}$ groups.

of strength one-third, since the bivalent metal has the co-ordination number six. It is therefore convenient, although in a sense arbitrary, to regard the Si—O bond as approximating to the strong, homopolar type, and the metal-oxygen bonds as being intrinsically weaker.

(B, ii) The process of cross-linking the strings of SiO_4 tetrahedra met with in the Si_4O_{11} anion may be extended yet a stage further, so that whole sheets of linked tetrahedra are formed. Each sheet is thus made up (Fig. 41) of indefinitely repeated Si_6O_{18} rings, and has a pseudo-hexagonal symmetry. The whole lamina, which has the gross composition $(\text{Si}_2\text{O}_5)^{2-}$, represents a macro-anion. Such silicon-oxygen sheets, being bound together by the strong valency forces discussed above, would be mechanically strong. Parallel sheets would be bound together more loosely through the weaker electrostatic bonds involving the cations, which must be packed between the sheets. The silicon-oxygen sheets should consequently coincide with pronounced cleavage planes of the crystal, and silicates with this type of structure should, conversely, exhibit

a well-developed laminar cleavage. Insertion of the known interatomic distances leads, as is shown in Fig. 41, to spacings for the unit cell which agree with the spacings in the cleavage plane as found for mica, talc, and those related minerals which have a

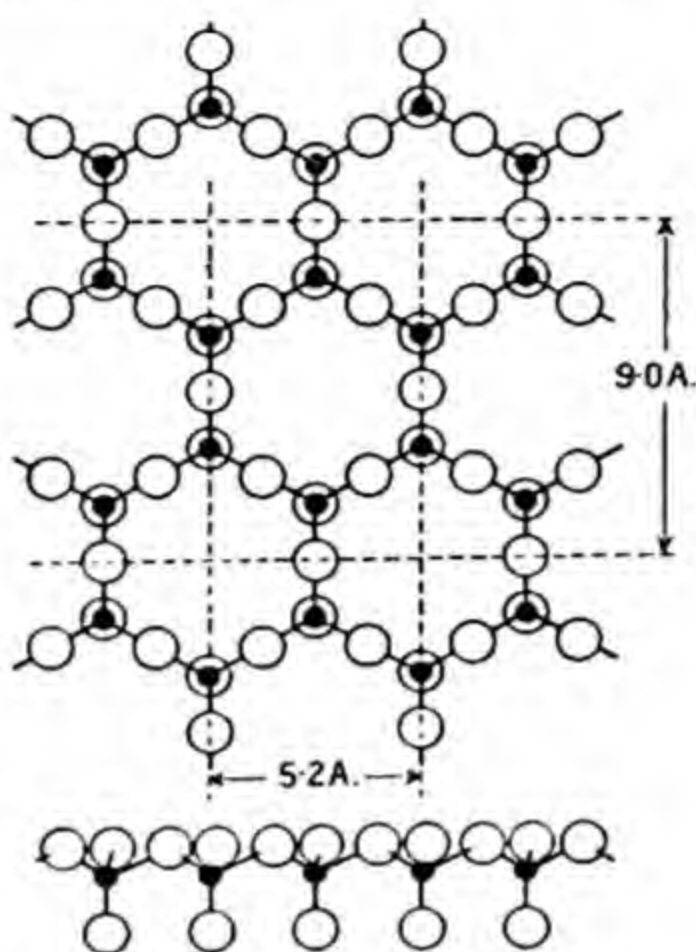


FIG. 41.—The formation of sheet-like silicon-oxygen networks.
The lower figure shows a cross-section of the sheet.

pronounced cleavage and pseudo-hexagonal symmetry. The long third principal spacing, of the order of 20 Å, found between the cleavage planes, corresponds to the weak bonding between the sheets.

Aluminosilicates.—While such a simple skeleton explains the most prominent features of the mica-like structures, it cannot be immediately applied in detail to the minerals of this group. They are not simple silicates, but aluminosilicates, in which aluminium enters into the composition of the sheets of linked SiO_4 tetrahedra by a process of isomorphous replacement of silicon. Pauling⁷⁶ has shown, however, that these and the clay minerals may be regarded as being built on a uniform sort of plan from superposed layers of $\text{Si}_2\text{O}_5^{2-}$ sheets (considered to be equivalent to single layers from the structure of β -cristobalite), of brucite, $\text{Mg}(\text{OH})_2$, and of hydrargillite or gibbsite, $\text{Al}(\text{OH})_3$, each layer being possibly modified by the process of isomorphous replacement. All the layer structures referred to are approximately identical in dimensions, being made by the insertion of the appropriate number of Si^{4+} , Mg^{2+} , or Al^{3+} ions into the interstices of a double layer of close-packed O^{2-} or OH^- ions. Thus, aluminium may replace a proportion of the silicon, or four atoms of aluminium may be replaced

⁷⁶ *Proc. Nat. Acad. Sci.*, 1928, 14, 603; 1930, 16, 123.

in turn by six atoms of magnesium. The composite layers are then formed by the sharing of oxygen atoms in the way shown by the schematic sections in Fig. 42.

In this way, Pauling advances for talc, $3\text{MgO} \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$, the structure represented in Fig. 42 (a). Layers of brucite are sandwiched, by the sharing of oxygen atoms, between two sheets of cristobalite, thereby making up composite layers which may be represented as $\dots \text{O}_6 \cdot \text{Si}_4 \cdot \text{O}_4(\text{OH})_2 \cdot \text{Mg}_6 \cdot \text{O}_4(\text{OH})_2 \cdot \text{Si}_4 \cdot \text{O}_6 \dots$. In pyrophyllite, $\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$ (Fig. 42 (b)), four aluminium atoms replace the magnesium of talc. The equivalence of the positive

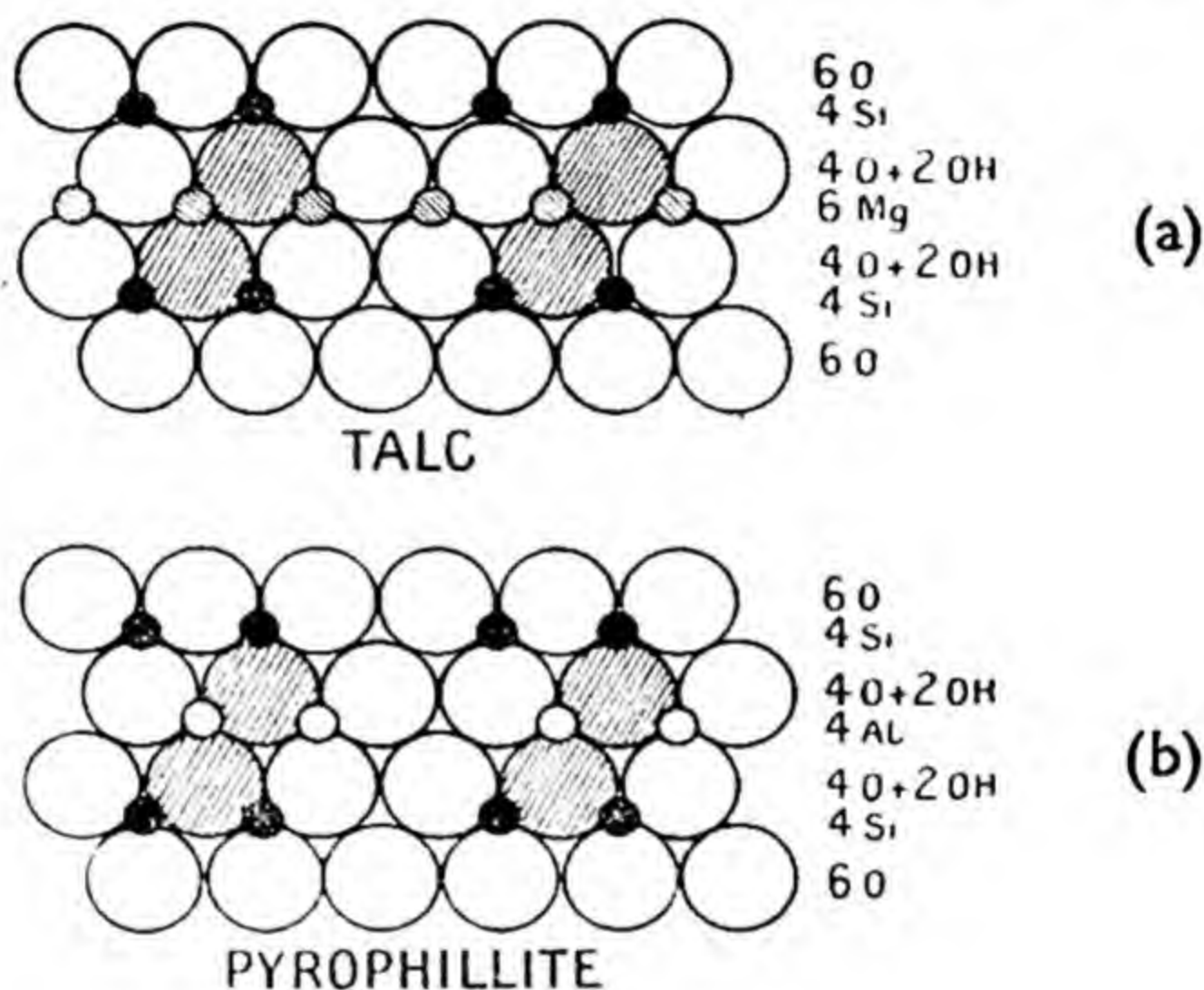
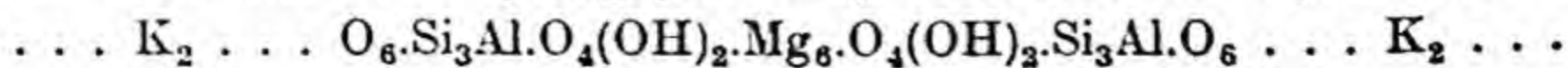


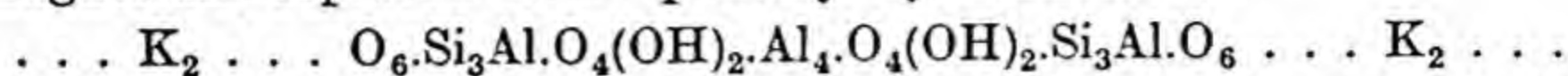
FIG. 42.

and negative ions in the composite sheet is thereby unaltered, but replacement of the magnesium by aluminium leaves one-third of the positions in the central layer unfilled. The gross composition is then given by $\dots \text{O}_6 \cdot \text{Si}_4 \cdot \text{O}_4(\text{OH})_2 \cdot \text{Al}_4 \cdot \text{O}_4(\text{OH})_2 \cdot \text{Si}_4 \cdot \text{O}_6 \dots$. In both of these structures each composite sheet is electrically neutral, so that the forces of interaction between the sheets are small. As a result, there is little resistance to slipping of one plane over the next, as is shown by the extreme softness of talc.

In phlogopite, $\text{K}_2\text{O} \cdot 6\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot \text{H}_2\text{O}$, a part of the silicon is replaced isomorphously by aluminium with the result that each composite layer bears a nett anionic charge. Alkali metal ions accordingly enter between the sheets in corresponding number. The constitution of phlogopite may therefore be represented as



Muscovite, ordinary mica, is structurally analogous, but with magnesium replaced isomorphously by aluminium:



Just as the isomorphous replacement of silicon in the cristobalite layers, atom for atom, by aluminium raises the anionic valency,

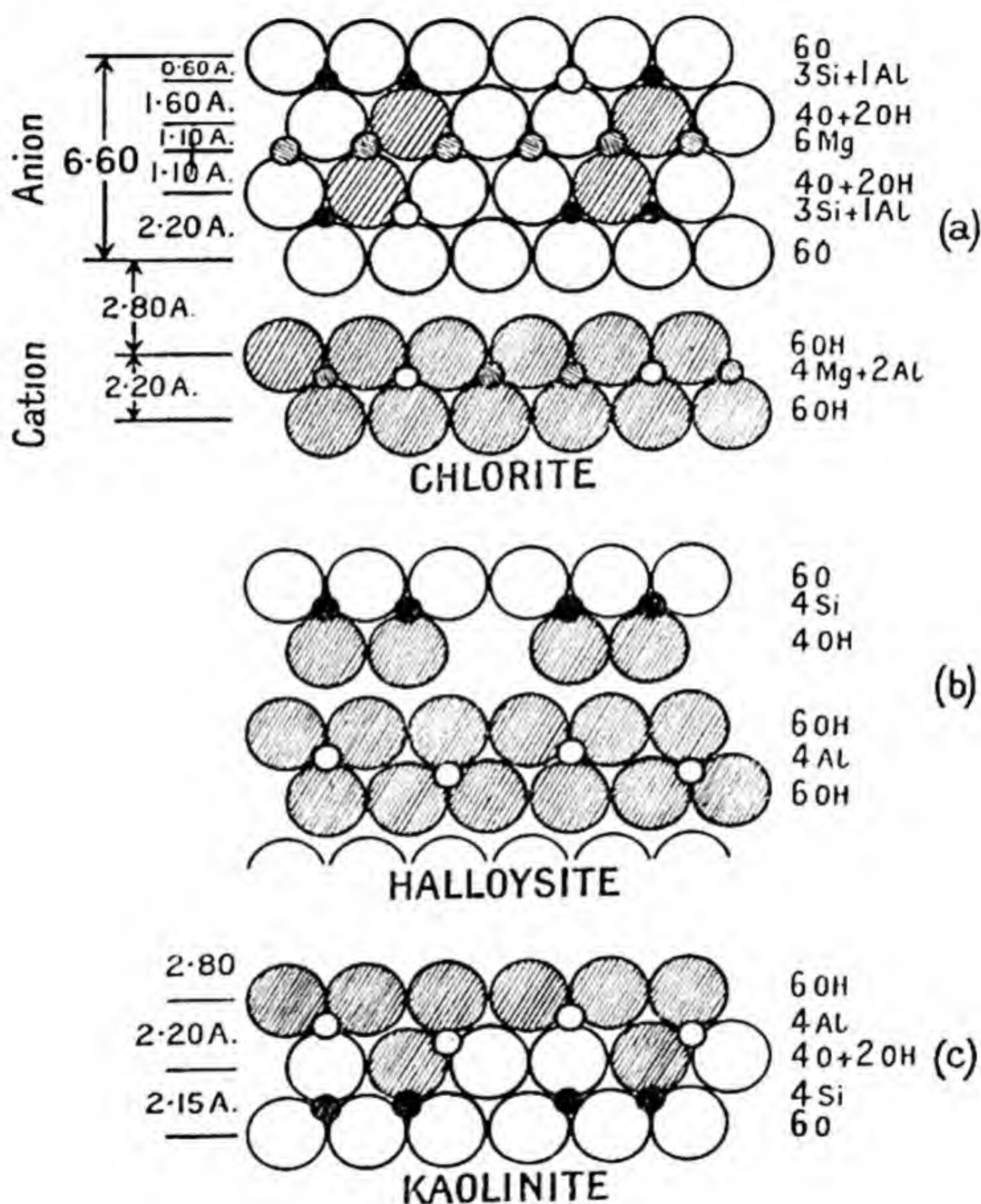


FIG. 43.

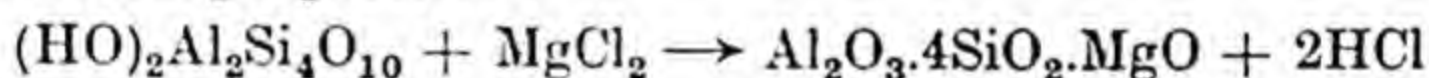
so the replacement of magnesium in brucite layers by aluminium raises the cationic valency. Chlorite, according to Pauling, is made up by interleaving mica-like anionic sheets with brucite-like cationic sheets (Fig. 43 (a)).

The gradation in properties as the structure is progressively varied is interesting. As has been pointed out, talc and pyrophyllite, with electrically neutral sheets, are very soft (hardness 1-2),

and as easily cleaved as graphite. In mica the charged layers are bound electrostatically through the interposed potassium ions, and so cleave less readily (hardness 2-3). Finally, in the brittle micas the charged anionic sheets are more tightly bound by doubly charged Ca^{2+} ions, in consequence of which the hardness is raised to 3.5-6, and the whole becomes brittle.

This theory of the mica group lacks as yet the rigid experimental backing possessed by Bragg's classification of the simple silicate structures. It does, however, provide a convenient and uniform basis for correlating the chemical composition and highly characteristic properties of these minerals with their crystal structure, and is compatible with the X-ray evidence. It can be regarded as a logical extension of the general principles emerging from Bragg's work, since it is based on the derivation of all silicate structures from an approximately close-packed arrangement of oxygen ions.

Chemical evidence which accords well with Pauling's views is afforded by Thilo's work on the high temperature reactions of pyrophyllite, $\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$, with metallic oxides and chlorides.⁷⁷ Thilo found that when pyrophyllite was heated with magnesium oxide or chloride at 700-1000°, water or hydrochloric acid was eliminated from the hydroxyl groups present, and that one atom of magnesium entered the compound for each two atoms of aluminium present, without any apparent change in the general structure and properties.



It has been shown above that the pyrophyllite structure is related to that of talc by replacement of six Mg^{2+} ions by four Al^{3+} ions, so that there should be just two vacant places in the central layer of each composite sheet for every four atoms of aluminium. This is in accord with the observations of Thilo, and suggests that any bivalent ion, normally six-co-ordinated, and of about the same size as Mg^{2+} , should be capable of being introduced in the same way, but not ions occurring normally in fourfold co-ordination. This is borne out by experiment. Ferrous iron, or cobalt, may be readily introduced in the same way as magnesium. On heating pyrophyllite with zinc oxide or zinc chloride, however, the whole structure is broken down to form the zinc spinel ZnAl_2O_4 , and zinc orthosilicate Zn_2SiO_4 , in both of which zinc can attain fourfold co-ordination. According to the Goldschmidt radius ratio rules, Ca^{2+} and Cd^{2+} should enter only into eight-co-ordinate structures, and so should not be capable of entering the pyrophyllite

⁷⁷ *Z. anorg. Chem.*, 1933, **212**, 369.

structure. This is again borne out by experiment, since calcium and cadmium chlorides were without action on pyrophyllite.

The Clay Minerals.⁷⁸—An important field in which Pauling's views have proved very fruitful is that of the minerals composing the clays. The isolation and identification of individual chemical species is here particularly difficult, but largely by the application of microscopic and optical methods of examination, the kaolinite group was first differentiated into kaolinite $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$, halloysite $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2-4\text{H}_2\text{O}$, and allophane $\text{Al}_2\text{O}_3 \cdot n\text{SiO}_2 \cdot m\text{H}_2\text{O}$. Of these, allophane has been shown to be amorphous, while the composition $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ has later been applied to three optically distinct species—kaolinite proper, nacrite, and dickite. A second important group of clays, the bentonites, which are characterized by their highly adsorbent and self-dispersing properties, contain as their major constituent montmorillonite. From analytical data, montmorillonite was originally formulated as $\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2 \cdot n\text{H}_2\text{O}$, with magnesium replaced partially by calcium, sodium or potassium. As will be seen, this formula has later been modified on the grounds of X-ray measurements. A second bentonite mineral is the highly colloidal beidellite (originally formulated as $\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 \cdot n\text{H}_2\text{O}$), which occurs also in many clay soils. Pyrophyllite, which is found crystalline in slates, is also included amongst the clay minerals. There is a group of clay constituents in which aluminium oxide is replaced wholly or partly by ferric oxide, and a complete isomorphous series exists between beidellite and nontronite, $\text{Fe}_2\text{O}_3 \cdot 3\text{SiO}_2 \cdot n\text{H}_2\text{O}$. In general, the iron clay minerals are less colloidal in properties than the aluminium minerals.

The X-ray study of the clays has shown that, except for the *c*-axis spacing, montmorillonite gives diffraction patterns identical with those obtained from pyrophyllite. The long *c*-axis spacing, which corresponds with the distance between the layers of the pyrophyllite structure, shows in montmorillonite an interesting and characteristic behaviour on dehydration. Montmorillonite absorbs considerable amounts of water, which must be packed between the pyrophyllite-like layers. The spacing between these layers depends entirely on the amount of water held by the structure, so that, on dehydration, the whole shrinks along the *c*-axis. The same unidimensional swelling and shrinkage, depending on the water content, is found also in nontronite.

From the identity of their diffraction patterns, it appears that the individual layers of pyrophyllite and montmorillonite should be similarly formulated as $\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O} + m\text{H}_2\text{O}$. This 'ideal'

⁷⁸ Cf. a review by C. E. Marshall, *Sci. Progress*, 1936, 119, 422.

formula differs from that based on chemical analysis, but Hofmann, Endell and Wilm⁷⁹ have suggested that aluminium may be in part replaced by magnesium after the manner already discussed, and that other bases may be adsorbed. It is, moreover, plain from Thilo's work on pyrophyllite that, by reaction with the hydroxyl groups, the introduction of extra magnesium ions into the gibbsite layer is conceivable.

Beidellite, from the X-ray evidence, is to be represented by the same ideal formula. It is not clear, on this basis, what differences account for the differing optical and physical characteristics of the minerals, nor whether they are to be accounted truly distinct compounds.

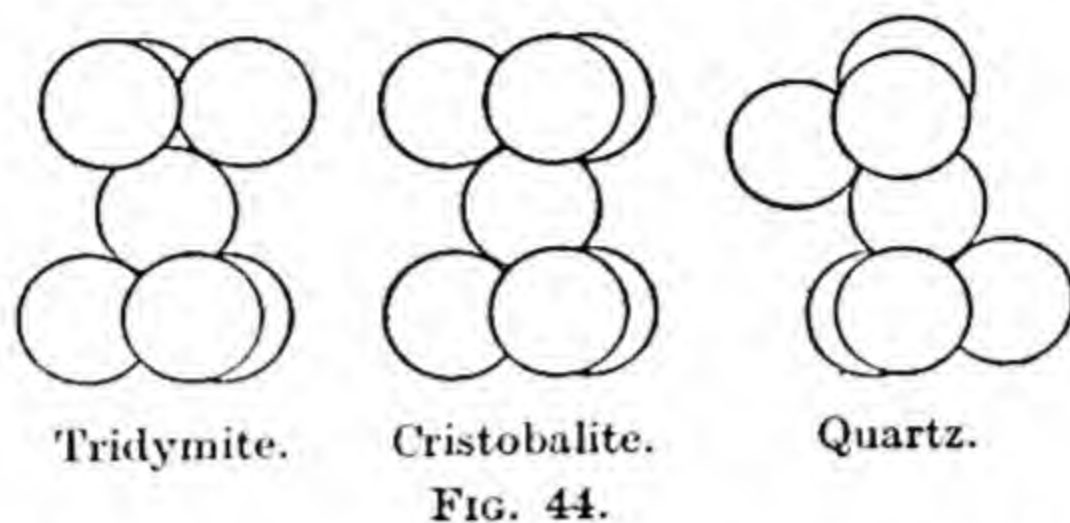
In halloysite, there appear to be alternating layers of hydrated silica, $\text{Si}_2\text{O}_3(\text{OH})_2$, and of gibbsite, $\text{Al}(\text{OH})_3$, so that the ideal formula is $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 4\text{H}_2\text{O}$. At 50° two molecules of water per unit of formula are lost, but the metahalloysite so formed is distinct from kaolinite, nacrite or dickite, which have the same gross composition. As may be seen from the schematic diagram (Fig. 43 (b) and (c)), kaolinite would be derived from halloysite by elimination of water between the gibbsite and silica hydrate layers.

While there are many points yet to be elucidated as to the structure of the clays, it is clear that a clue has been found to the understanding of some of their outstanding physical properties. The layer lattice structure is broken down by the entry of water—as evidenced by the unidimensional swelling of montmorillonite—into laminae which, theoretically, might, in the limiting case, be macromolecules one layer thick. In any case, thin, flaky particles are formed, which account for the thixotropic properties of the clay slip, while the ease of displacing the electrically neutral layers over one another must, in itself, confer an added plasticity. The hydrophilic nature of the clays, and their shrinkage on drying, can, in turn, be correlated with the way in which variable amounts of water may be introduced between the planes, causing a unidimensional expansion of the whole lattice.

(C) *Three-dimensional Networks*.—If the process of oxygen-sharing is extended, so that each sheet is linked to the neighbouring sheets above and below, a network is obtained in which every oxygen atom is common to two tetrahedral SiO_4 groups. The whole network then has the composition SiO_2 , and represents one giant molecule of silica. The three principal crystalline forms of silica—cristobalite, tridymite, and quartz—are based on this kind

⁷⁹ Z. Krist., 1933, 86, 340.

of structure.⁸⁰ Cristobalite and tridymite are built up in exactly the manner described, and differ in the way the cross-linking is achieved. In quartz; the regular arrangement is somewhat distorted, so that spirals of O—Si—O—Si—O— chains lie around trigonal screw axes of symmetry (Fig. 44).



Felspars, Zeolites, etc.—The three-dimensional silicon-oxygen framework is electrostatically neutral, but as in the structures already considered, the Si^{4+} ions, around which the oxygen tetrahedra are centred, may be replaced by Al^{3+} ions. As each such substitution leads to one unbalanced anionic charge, positive ions must be introduced to maintain electrical neutrality. According to Machatski,⁸¹ this is the essential structure of the felspars and zeolites.

The resulting network, as will be understood from the preceding sections, involves rings of tetrahedra (with the gross formula such that $\text{Al} + \text{Si} : \text{O} = 1 : 2$), built up by sharing vertices, so that they form an extended honeycomb-like structure, of high symmetry, with wide channels through the rings, and cavities in the honeycomb structure. To this kind of open framework are due the characteristic properties of the felspar type of aluminosilicates, including the zeolites and ultramarines. The two most striking general properties of these substances are their capacity for base-exchange, and the ability of the hydrated materials to lose water or to rehydrate without undergoing any change in optical or crystallographic properties. By 'base-exchange' is meant the replacement in these substances of one cationic constituent by another, on simple treatment with a salt of the corresponding metal. Thus, if a sodium zeolite such as analcite, $\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$, be treated with a solution of a salt of some other metal—e.g. silver nitrate—the sodium is replaced by an equivalent amount of the second cation, giving a silver zeolite in the case quoted. The reactions concerned are reversible and lead to a state of equilibrium.

⁸⁰ R. E. Gibbs, *Proc. Roy. Soc.*, 1925, A, 109, 405; 1926, 110, 443; 1927, 113, 351.

⁸¹ *Zentr. Min.*, 1928, A, 97.

The possibility of base exchange in this manner must be associated with the open-work structure of the crystal, down the channels of which cations may wander. Replacement of one cation by another is then readily possible, and can take place without affecting the nature or dimensions of the crystal lattice.

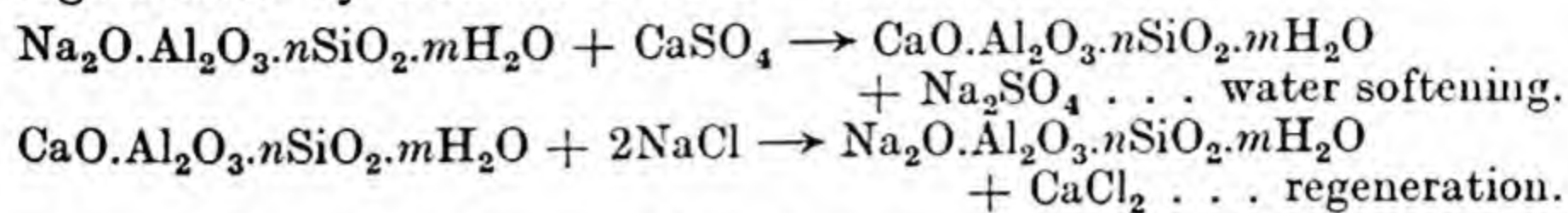
The diffusion of water into the cavities of the crystal lattice can also take place down the channels of the structure, and since the water molecules do not play an important structural role, dehydration and rehydration can take place without the formation of a second solid phase. The partially dehydrated zeolite thus constitutes a bivariant system from the standpoint of the phase rule, and the dissociation pressure varies with the water content. As might be expected, the dehydrated zeolites have a considerable absorptive power for gases other than water vapour. In the process of absorption and desorption the molecules must pass along channels of literally molecular dimensions, having a diameter determined by the crystal structure itself. This feature confers on certain zeolites—notably chabazite and mordenite—the remarkable property of acting as *molecular sieves*, permeable to certain gases only.⁸²

Thus Barrer has shown that chabazite and gmelinite, in which the narrowest cross-section of the interstitial channels lies between 4.9 and 5.6 Å, will occlude methane and ethane rapidly, and *n*-paraffins slowly, but cannot occlude branched chain paraffins or aromatic hydrocarbons. Mordenite rich in sodium, with smaller channels (4.0–4.9 Å), takes up no hydrocarbon molecules larger than ethane, and absorbs methane and ethane only slowly, whereas nitrogen, oxygen and smaller molecules are occluded rapidly. The replacement of sodium in mordenite by calcium or barium (by a cation exchange process) decreases the cross-section of the channel to 3.8–4.0 Å. Such mordenites will absorb nitrogen, argon and smaller molecules, but not methane or ethane. The process of absorption involves the diffusion of the gas molecules through the solid, and it is the activation energy of this process which, varying from one molecule to another, confers selectivity. By operating at appropriate temperatures the selective occlusion can be utilized to effect difficult separations of gaseous mixtures—thus *n*-heptane and *iso*-octane can be separated quantitatively. It may be noted that the vitreous silicates—silica glass and Pyrex glass—exercise a molecular sieve effect, being permeable only to helium at moderate temperatures.

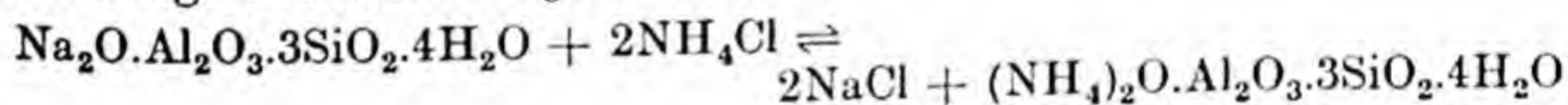
Synthetic Zeolitic Bodies.—The same phenomenon of base exchange is exhibited also by certain synthetic silicate masses, notably by those materials manufactured under the name of 'Permutit', and is applied, as is well known, to the softening of water. In this

⁸² See the review by R. M. Barrer, *Chem. Soc. Quarterly Rev.*, 1949, 3, 293.

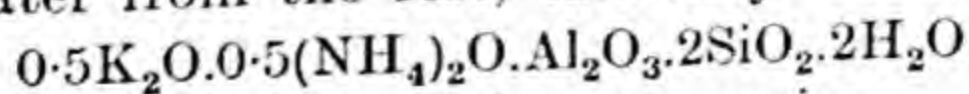
case, the calcium salts present in the water undergo base exchange with a sodium zeolite, whereby dissolved calcium is replaced by sodium. As the concentration of calcium in the water-softening mass increases by progressive exchange, the material may be regenerated by treatment with sodium chloride:



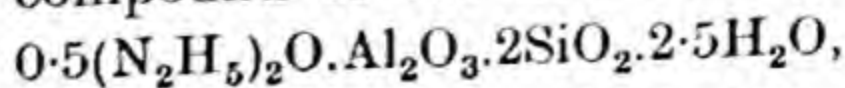
These artificial base-exchanging zeolites, which are sodium aluminosilicates of the general formula $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot n\text{SiO}_2 \cdot m\text{H}_2\text{O}$, would appear from their chemical properties to be built upon a general structural model similar to that obtaining in the natural zeolites. As the proportion of silica is increased, the physical properties change; the ease of base exchange is lost, and the materials become brittle and glassy when n is greater than 3. The silica-rich substances—*e.g.* those with $n = 3$ or 4, $m = 4$ —appear to be derived from the one basic compound $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ by combination with, or inclusion of, approximately stoichiometric amounts of orthosilicic or metasilicic acids. They are degraded into the parent substance, sodium metasilicate and silicic acid when they are hydrolysed with 10 per cent caustic soda under pressure. Whereas the silica-rich substances interchange normally in base exchange reactions—*e.g.*



—the supposed parent compound interchanges abnormally with the ammonium ion.⁸³ It gives, instead of the ammonium zeolite of analogous formula, a new type, $0.5(\text{NH}_4)_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2.5\text{H}_2\text{O}$. Similar results are obtained by base exchange with hydrazine salts. The new type of structure so obtained exchanges normally with neutral salt solutions, forming, for example, $0.5\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2.5\text{H}_2\text{O}$, $0.5\text{Tl}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2.5\text{H}_2\text{O}$, but with alkalis a salt of the original series is re-formed. In the presence of ammonia, base exchange with neutral salts introduces the new cations without displacing the ammonium; potassium salts thus give $0.5\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2.5\text{H}_2\text{O} \cdot \text{NH}_3$ or, differentiating one-half molecule of water from the rest, this may be written as

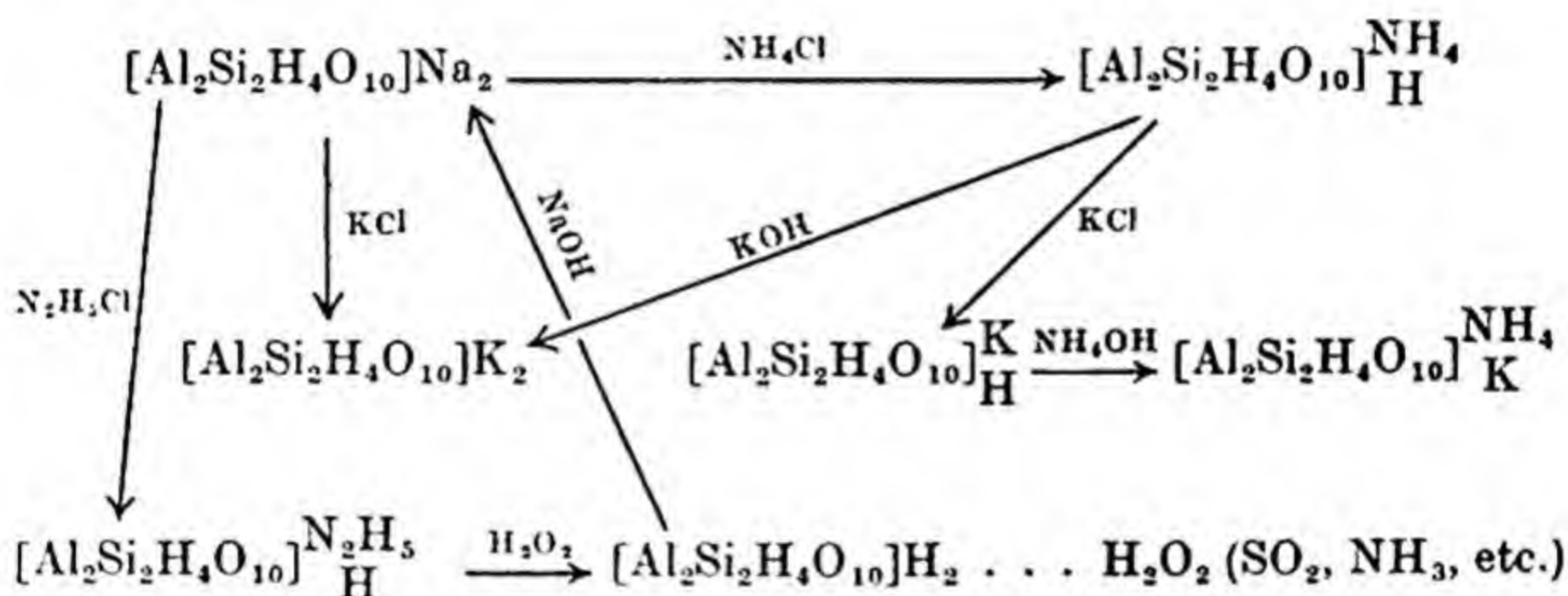


The hydrazine compound of the new series,

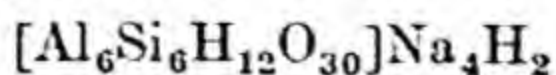


⁸³ Gruner and Hirsch, *Z. anorg. Chem.*, 1931, 202, 337; Gruner, *ibid.*, 1931, 202, 358.

may be oxidized with hydrogen peroxide, forming a compound $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O} + \text{H}_2\text{O}_2$; this contains hydrogen peroxide, which may be displaced by sulphur dioxide to give $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O} \cdot \text{SO}_2$. It is possible to introduce water or ammonia in the same loosely attached way. When these compounds are heated at 125° with water, sulphur dioxide or hydrogen peroxide are lost, and the product, $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O}$, is free from any cations. The substance so obtained does not undergo base exchange reactions with neutral salts, but caustic soda reacts with it to form the sodium compound $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$. The extra molecule of water in the base-free compound thus represents the hydrogen which is replaceable by cations, and the base-free compound is the parent acid of a series of compounds based on the structural unit $[\text{Al}_2\text{Si}_2\text{O}_{10}\text{H}_4]^{2-}$. The whole series of reactions may then be summarized in the table below.



Further evidence as to the fundamental structural unit of the compounds is afforded by the following considerations. The aqueous suspensions of the sodium compounds are alkaline in reaction, due to hydrolysis. By titrating the alkali so liberated in such a way that the solution is kept always on the alkaline side of neutrality it may be shown that exactly one-third of the sodium is hydrolysed out, leaving a residue of the composition $\frac{2}{3}\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\frac{1}{3}\text{H}_2\text{O}$. This would imply that the formula should be tripled throughout; the sodium compound can then be expressed as $[\text{Al}_6\text{Si}_6\text{H}_{12}\text{O}_{30}]\text{Na}_6$, which hydrolyses to



The conclusion is thus reached, on purely chemical grounds, that in these compounds the typical base exchange properties are associated with a unit containing a total of twelve aluminium and silicon atoms. An immediate analogy is thereby suggested with those natural zeolites and related compounds, where just such a

dodecahedral unit of structure, infinitely repeated throughout the crystal, is responsible for the full development of zeolitic properties. In the artificial zeolites, the anion is probably finite in size, so that the relation

$$(\text{number of oxygen atoms in unit}) = 2 \times (\text{Al atoms} + \text{Si atoms}),$$

which obtains for the perfect aluminosilicate network, no longer applies.

Ultramarine.—Amongst the most interesting of the aluminosilicate minerals is the blue sodium aluminosilicate, containing sulphur, known as ultramarine. The problems of its constitution, and of the origin of the deep colour in such a compound, are not yet entirely solved, although, as will be seen, much has been done in recent years to elucidate its structure.

The deep blue mineral lazurite, called lapis lazuli in mediæval times, has been known and prized as a semi-precious gem since the classical era. It is very often interspersed with specks of pyrites—mistaken by the ancients for spangles of gold—in consequence of which Pliny (A.D. 70) and others long before him likened it to the deep blue night sky, with its multitude of glistening stars. The sapphire, referred to in the Bible, and described by Theophrastus, may be identified with the lapis lazuli. From the Middle Ages onwards, lapis lazuli was imported into Europe from the East, as a stone for mosaics and as a highly prized pigment; as being imported from abroad it became known as 'azurum ultramarinum'—the blue from beyond the seas. The most valuable deposits of lazurite were in Asia, especially at Badakshan in Afghanistan. Thence the stones were brought by way of Persia or Bokhara and Russia to the markets of Europe. Marco Polo, in 1271, described the process by which the pigment was extracted from the stone.

The value placed upon ultramarine as a pigment led to many attempts to prepare it artificially. Following the chemical analysis of ultramarine by Clément and Désormes in 1806, a prize was offered in France for an economically practicable process for the production of synthetic ultramarine: this prize was won in 1828 by Guimet, and the ultramarine of commerce is to-day entirely of artificial origin. By suitable control of the manufacturing process it is possible to prepare ultramarines of any shade from white or pale blue-green to red or violet.

In principle, the manufacture of ultramarine consists in heating kaolin to redness in the absence of air with sulphur or sodium sulphate and carbonaceous reducing agents. A yellow-green mass is thereby obtained, which is reheated in air; the colour deepens,

and finally becomes dark blue. Soluble sodium salts are then leached out, leaving the pigment. The three main variations of the process are (a) the sulphate process, in which kaolin (or pottery clays approximating in composition to kaolin) is heated with sodium sulphate and wood charcoal; (b) the soda-sulphate process, using a mixture of kaolin with sodium sulphate, sodium carbonate, sulphur and tar; and (c) the soda process, which uses a mixture of the silicate with sodium carbonate, sulphur, colophonium and tar. These variants are listed according to the order of increasing depth of colour, alkali and sulphur content of the product.

The composition of the ultramarines is very variable and never stoichiometric, but according to R. Hoffmann, the 'ideal' compositions of the products obtained by each of the three processes are:

sulphate process	sulphate-soda process	soda process
$\text{Na}_{10}\text{Al}_6\text{Si}_6\text{O}_{24}\text{S}_2$ white	$\text{Na}_{12}\text{Al}_6\text{Si}_6\text{O}_{24}\text{S}_3$ white	$\text{Na}_{14}\text{Al}_6\text{Si}_6\text{O}_{24}\text{S}_4$ white
$\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{S}_2$ green	$\text{Na}_9\text{Al}_6\text{Si}_6\text{O}_{24}\text{S}_3$ green	$\text{Na}_{10}\text{Al}_6\text{Si}_6\text{O}_{24}\text{S}_4$ green
$\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24}\text{S}_2$ blue	$\text{NaAl}_6\text{Si}_6\text{O}_{24}\text{S}_3$ blue	$\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{S}_4$ blue

while lapis lazuli itself is $\text{Na}_{10}\text{Al}_6\text{Si}_6\text{O}_{24}\text{S}_6$. Ultramarines of a deeper colour may be obtained in which the ratio Al : Si approximates to 1 : 1.5. These have a greater resistance towards decolorization by alum solutions than have the ultramarines with Al : Si = 1 : 1.

As with the zeolites, the alkali in ultramarine is exchangeable for other bases.⁸⁴ Thus, the blue sodium compound reacts with silver nitrate, giving a yellow silver ultramarine, from which, by the action of metallic salts, ultramarines containing a variety of other metals may be prepared. As is the case also with the zeolites, the degree to which exchange takes place is highly variable, and depends on the concentration of the solutions, the time of heating and similar factors. It is important to note, however, that whether high-silica or low-silica sodium ultramarines be taken, the silver ultramarines derived from them, according to Jaeger, invariably have Al : Si = 1 : 1—an observation which materially supports Hoffmann's formulation of the aluminosilicate skeleton.

Ultramarine is fairly stable towards alkalis, but acids break down the sulphur-containing part of the molecule, with the liberation of sulphur and hydrogen sulphide. The proportion of the latter product measures the so-called 'degree of reduction' of the sulphur. Water under pressure at 300° extracts sodium sulphide and leaves a colourless residue. A regulated acid decomposition is

⁸⁴ For a summary, see F. M. Jaeger, *Trans. Faraday Soc.*, 1929, 25, 320.

provided by the action of ethylene chlorhydrin which at its boiling-point removes alkali without any loss of sulphur or change in the degree of reduction of the sulphur. During this process, the colour changes to pink and finally to white. Protracted treatment in this way removes practically all the alkali, and ultimately destroys the crystal lattice.⁸⁵ The alkali may be re-introduced by treating the partially extracted material with various reagents; the white product is turned green by aqueous sodium sulphide, and pale blue by fusion with sodium sulphide. Sodium hydroxide turns it yellow, and effects some decomposition by extracting sodium polysulphide. On fusion with sodium nitrate at temperatures below 550° , up to 12.5 per cent of sodium may be acquired without any loss of sulphur, the colour changing to a strong yellow-green. If, now, the excess of sodium nitrate be removed, the product forms a deep blue crystalline ultramarine when it is heated in a limited supply of air, but not when it is heated either in pure nitrogen or in pure oxygen. A regulated degree of oxidation thus seems to be necessary, in accordance with the view that regards the colour as due to incomplete oxidized sulphur compounds (see p. 257).

The colour of ultramarine is also destroyed by fusion with sodium formate, and a white reduction product is obtained which contains more sodium, and yields twice as much hydrogen sulphide as does ultramarine on treatment with acids. X-ray examination shows, however, that the ultramarine crystal lattice remains intact. Reagents which remove the excess of alkali from this reduced substance—*e.g.* ethylene chlorhydrin, hydrogen chloride gas, hot water—restore also the blue colour, which is regained also when the substance is heated above 200° either in air or in a vacuum. The colour change on heating is therefore not associated with any process of oxidation.

In the same way, chlorination of ultramarine at 400° removes alkali and gives colourless products. If the process be stopped before destruction of the crystal lattice takes place, a colourless product is obtained, which regains its blue colour on fusion with alkali. It appears, therefore, that the alkali in ultramarine is more mobile than is the sulphur, and that either excess or deficiency of alkali can destroy the colour.

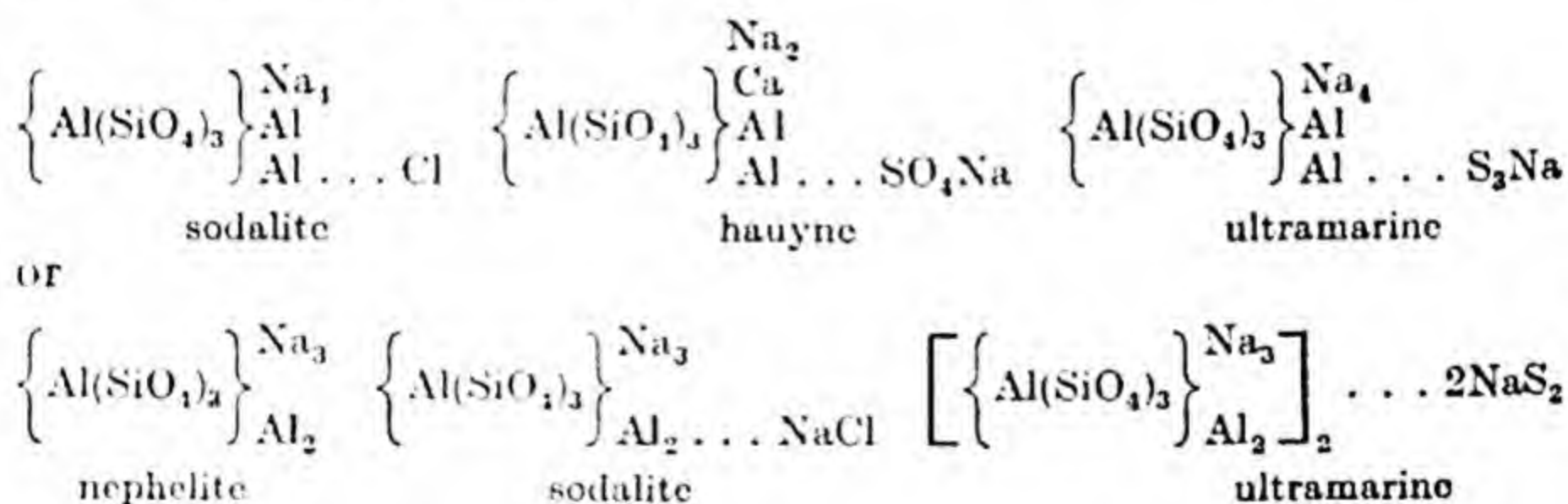
Attempts to investigate the manner in which the sulphur is present have been made by Leschewski and Möller.⁸⁶ Hydrogen reduces ultramarine at 400° , giving a pale blue product which

⁸⁵ Leschewski and Möller, *Z. anorg. Chem.*, 1932, 209, 369; 1934, 220, 317.

⁸⁶ Leschewski and Möller, *Z. anorg. Chem.*, 1933, 212, 420; 1932, 209, 377; *Ber.*, 1932, 65, 250.

retains the ultramarine crystal lattice. During the reduction little sulphur is lost, but the degree of reduction is increased—*e.g.* in an ultramarine with 7.8 per cent of sulphur, the sulphide sulphur was so raised from 0.9 per cent to 6 per cent. Above 400° , more sulphur is lost as hydrogen sulphide, and the colour again deepens. The converse process, oxidation with oxygen at 500° , lowers the degree of reduction of the sulphur, but does not destroy either the crystal lattice or the colour. Alternate oxidation and reduction with oxygen and hydrogen respectively yields alternate dark blue and light blue products.

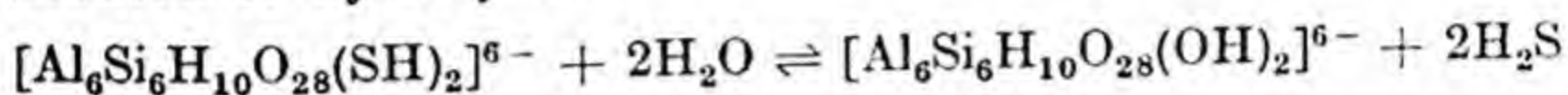
The properties of the ultramarines suggest that they must be related to the naturally occurring base-exchanging minerals, and especially—as observed by Brögger and Backström in 1890—to sodalite, $\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{Cl}_2$, nosean or haüyne, $\text{Na}_4(\text{Na}_2, \text{Ca})\text{Al}_6\text{Si}_6\text{O}_{24}(\text{SO}_4)_2$, and cancrinite, $(\text{Na}_2, \text{Ca})_5\text{Al}_6\text{Si}_6\text{O}_{24}(\text{CO}_3)_2$. All of these have been regarded as addition compounds of a sodium aluminosilicate with NaCl , Na_2SO_4 (or CaSO_4) and Na_2CO_3 , respectively. Ultramarine thus appears similarly as formed by the addition of sodium polysulphide to the same parent aluminosilicate. Alternatively, nephelite has been regarded as the parent compound of this group. The relation between the different substances is then illustrated by the following alternative formulations (in which the formulæ are halved for simplicity):



The analogy with the zeolites is supported by the observations of Singer and of Gruner,⁸⁷ as to the action of alkali sulphides on synthetic zeolites. Blue substances are so formed, the colour being particularly deep in the case of the alkaline earth compounds. In contradistinction to the true ultramarines, however, these substances are not very stable. Sulphur may be removed by washing, with decolorization of the material, and hydrogen sulphide is liberated when they are dried either at 100° or at the ordinary temperature. The amount of sulphur taken up varies from 3 to 4 atoms for each

⁸⁷ *Z. anorg. Chem.*, 1932, 204, 232, 247.

formula weight of $\text{Na}_6[\text{Al}_6\text{Si}_6\text{H}_{12}\text{O}_{30}]$ (see above for Gruner's formulation of the artificial zeolites). Since the acid equivalent of the material is unchanged by the treatment with alkali sulphide, it is inferred that S^{2-} or SH^- ions are taken up as such, although oxidation of sodium sulphide to polysulphide is also possible. That some such oxidation occurs, and is associated with the development of colour, is shown in that treatment of a thoroughly out-gassed zeolite with sodium sulphide in an atmosphere of nitrogen yielded a colourless product containing exactly two atoms of sulphur per molecule of $\text{Na}_6[\text{Al}_6\text{Si}_6\text{H}_{12}\text{O}_{30}]$. The sulphur is considered to enter the molecule by the direct exchange of SH^- for OH^- groups giving $[\text{Al}_6\text{Si}_6\text{H}_{10}\text{O}_{28}(\text{SH})_2]^{6-}$. The loss of sulphur during drying is then attributed to hydrolysis:



In the presence of air, sodium hydrosulphide is readily oxidized to polysulphide, so that the reaction with zeolites in aerobic conditions might easily lead to the introduction of S_2H^- or S_2^{2-} groups. Blue substances of much greater stability, more closely related to the true ultramarines, are obtained by the action of sodium sulphide solutions at temperatures above 200° , under pressure. These, like the true ultramarines, catalyse the reaction of iodine with sodium azide; they give clearly defined X-ray diffraction patterns identical with or very similar to those obtained from true ultramarines.

X-ray evidence as to the constitution of ultramarine was first advanced by Jaeger,⁸⁸ who showed that the 'powder' photographs obtained from all ultramarines, quite irrespective of their colour and chemical constitution, were identical amongst themselves and with the diffraction patterns given by nosean and haüyne. Soda-lite,⁸⁹ however, gave entirely different diffraction patterns, and should therefore not be grouped with nosean and ultramarine in the manner discussed above. Variation in the cations of ultramarine—*e.g.* replacement of sodium by silver—caused only alterations in the relative intensities of the different reflexions, without any significant changes in spacing. There is a minor effect on the dimensions of the structure, in that the insertion of a smaller cation (*e.g.* substitution of lithium for sodium) causes a slight shrinkage of the whole aluminosilicate skeleton. The sulphur of ultramarine may be replaced by selenium with no effect on the structure other than a similar alteration in relative intensities.

The structure of the compounds is based on a body-centred cubic

⁸⁸ Ref. 84; *Proc. Acad. Amsterdam*, 1927, 30, 249.

⁸⁹ See Pauling, *Proc. Nat. Acad. Sci.*, 1930, 16, 453.

lattice, of 9.13 Å side. The unit cell contains twenty-four atoms of oxygen, with six atoms of silicon and six of aluminium. The observed symmetry of this $[\text{Al}_6\text{Si}_6\text{O}_{24}]^{6-}$ unit demands that it should form a regular octohedral unit in the three-dimension (Si,Al)—O framework, with the wide channels and vacant cavities characteristic of the zeolites. Jaeger could not locate the cations or the sulphur atoms in this structure, and suggested that these could wander through the lattice, occupying random or indeterminate positions. Newer studies of the structure show, however, that there is no need for such a view.

According to Podschus, Leschewski and Hofmann,⁹⁰ the ideal formulæ for the ultramarines and related compounds given above must be modified, in that there is no room for more than eight large cations such as Na^+ in each unit cell. Higher contents of sodium must be interpreted as due to admixed sodium salts. In the ultramarines themselves there are invariably less than eight atoms of sodium—a typical material analysed by them had the composition $\text{Na}_{6.63}\text{Al}_{5.87}\text{Si}_{6.13}\text{O}_{24}\text{S}_{2.45}$, with $\text{Al} + \text{Si} = 12$, as the theory demands. There are places for eight cations in the crystal structure, and it is suggested that the sodium ions are distributed statistically over the available places. The sulphur probably is present in the form of S_2 groups, which may well be polysulphide ions. These are relegated to octohedral groups occupying the centre and corners of the unit cubic cell. Of these groups, again, not more than two of the six possible positions are occupied, and considerations of the actual space available for occupation by the sulphur make it improbable that any polysulphide groups larger than S_3^{2-} can be present.

It is plain from the foregoing section that the ultramarines are closely related structurally to the zeolites; the origin of their colour remains to be discussed. The chemical evidence shows that the colour is associated with the presence of regulated amounts of alkali and of sulphur, which latter must be present in part as sulphide ions, the remainder being probably polysulphidic. Older theories⁹¹ attributed the blue colour to colloidal sulphur. Thus coloured products containing colloidal sulphur are obtained from ferric chloride and sodium thiosulphate, or by the addition of sulphur to fused sodium or potassium chlorides. Fused potassium thiocyanate also develops a blue coloration.

Substances which have been supposed to be related to the ultramarines are obtained by fusing borax with sodium sulphide or

⁹⁰ *Z. anorg. Chem.*, 1936, 228, 305.

⁹¹ K. A. Hofmann, *Ber.*, 1905, 38, 2482; Wo. Ostwald and Auerbach, *Kolloid Z.*, 1926, 38, 336; see also Ref. 92.

sulphur.⁹² Yellow, red and dark brown colorations are developed, which darken to green or blue on the addition of boric acid. The higher polyborates—*e.g.* $\text{Na}_2\text{B}_{10}\text{O}_{16}$ —give blue melts when they are treated in solution with hydrogen sulphide and subsequently fused: the colour is deepened by heating the products in carbon disulphide vapour. Boric acid in these so-called 'boron ultramarines' may be partially replaced by alumina or silica, while sulphur may be replaced by selenium, giving pink to brown colours, or by tellurium, which gives greys or blacks. Hydrated sodium sulphide gives an analogous sky-blue melt with sodium phosphate and phosphorus pentoxide. All these colours, however, are transient and unstable. They may well be due to highly disperse colloidal sulphur, and Wo. Ostwald and Auerbach sought to extend the hypothesis to the true ultramarines, correlating the variation in colour with different degrees of dispersion of the colloidal sulphur. Their view is not acceptable, however; Podschus, Leschewski and Hofmann consider that the crystal structure excludes any possibility of colloidal particles being present, and—as has been seen—the sulphur is completely non-volatile and resistant to oxidation in nitrate melts up to 550° . The true origin of the intense blue of the ultramarines is thus still unexplained, although its association with the presence of polysulphide sulphur is certain.

The Formation of Natural and Artificial Silicates.

The structural chemistry of the silicates is based almost entirely on the multiplicity of compounds represented amongst the naturally occurring silicates. These are remarkable both for the complex organization of the structures found in many of them and for the perfection with which they have crystallized. It has been the task chiefly of the mineralogist to work out the conditions under which the different classes of silicate were formed, and the conclusions reached suggest that certain principles underlie the sequence of nucleation and growth of alternative structures from a complex system.

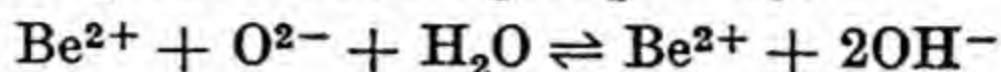
It is accepted that the minerals were derived originally from a fluid silicate melt, or magma. Chemically, this was a multi-component system, with the oxides of silicon, aluminium, calcium, magnesium, iron, sodium and potassium as main components, but with numerous minor constituents also. In particular it contained a small amount of water which—in the intermediate range of temperature, at least—was probably combined in the same fashion as water is retained in a metaphosphate melt (*q.v.*). The solid compounds deposited at high temperatures were those containing no

⁹² *Z. anorg. Chem.*, 1929, 183, 37.

water, which thus increased in concentration in the liquid phase as solidification proceeded. The partial pressure of water vapour in the system rose in consequence, and the nature of the liquid phase changed progressively from a mobile melt, through a highly viscous liquid, subjected to the action of super-critical water vapour, and ultimately to an aqueous solution in the critical region and below.

Under these conditions, the solids deposited showed a regular progression. Not only did the ratio of acidic oxides to basic oxides increase as the temperature fell and solidification progressed (corresponding to the transition from basic to acidic rocks), but there were successively traversed the principal structural types reviewed in this chapter. From natural magmas, the first substances crystallizing were not silicates, but heavy metal oxides (magnetite, chromite, etc.), but the first silicates to crystallize were the orthosilicates (*e.g.* olivine), to be followed at lower temperatures by the metasilicates (pyroxenes). The ordering process, as between melt and growing crystals, thus gave rise first to structures with island anion groups, and then to the one-dimensional extended structures. The formation of three-dimensional network structures—quartz, aluminosilicates of feldspar type—and of the sheet structure aluminosilicates (micas) represented the third stage in the crystallization of the silicates, and occurred under conditions such that water vapour, now present in rapidly increasing concentration, could participate in the surface reactions between melt and solid, thus acting as a mineralizing agent. In the final stages of crystallization there was present a supercritical aqueous solution of all the components soluble under such conditions. Whereas the preceding stages led essentially to compounds based on the close packing of ions (corresponding to the close packing in the melt from which crystallization took place), the conditions of the so-called hydrothermal crystallization produced the complex open-work structures of the zeolites and related bodies. These represent the products of reaction between the solution phase and aluminosilicates previously deposited. As would be expected, there is a regular trend from the completely anhydrous silicates deposited at the highest temperatures to those in which water and OH^- ions play an increasing structural role. Finally, the important group of clay minerals is of secondary origin, formed at the ordinary temperature by the action of weak acids (CO_2 and humic acids) on aluminosilicates such as feldspar and mica. Their important physical properties are typically the results of their formation by topochemical processes. The chemical mechanism of their formation cannot be stated: it should repay a detailed study.

halogen character, and high polarizability, of the OH^- ion. The elements involved are those which form volatile, or fairly volatile, chlorides which, as isolated molecules, have covalent character. Water vapour is strongly chemisorbed on oxide surfaces, and is doubtless held in part as OH^- groups—*e.g.*



on the surface. The hydroxides of these elements are unstable at high temperatures, so that water is in general desorbed by reversal of the above reaction. Alternatively, if a Be^{2+} ion chances to have two OH^- ions adjacent to it, it is plausible to suppose that a covalent $\text{Be}(\text{OH})_2$ molecule might evaporate from the surface. In the gas phase this may be a stable entity, though readily decomposed, reforming the oxide, by collision with a surface. On this view, beryllia and silica volatilize as $\text{Be}(\text{OH})_2$ and $\text{Si}(\text{OH})_4$, the latter existing only in the gaseous phase.

CHAPTER VIII

HYDROGEN AND THE HYDRIDES

The chemist's interest in hydrogen has been revived in recent years by two discoveries of outstanding importance, namely, the occurrence of spin isomerism in the hydrogen molecule, as a result of which ortho and para hydrogen exist, and, secondly, the existence of isotopes of hydrogen. It is proposed to review each of these topics in turn in this chapter before dealing with the much wider subject of the preparation and properties of the hydrides and of certain related compounds.

Ortho and Para Hydrogen.

The existence of two forms of molecular hydrogen, which are known as ortho and para hydrogen, arises from the fact that in a hydrogen atom the nucleus is spinning like a top, its angular momentum being $\frac{h}{4\pi}$.¹ When two such nuclei combine to form a molecule the spins can be either in the same direction, or in opposite directions. When in the same direction, as in the diagram below, they are said to be antisymmetrical, and the resulting hydrogen molecule is called ortho hydrogen. When they are in opposite directions, they are said to be symmetrical, and the molecule is called para hydrogen. This type of spin isomerism will exist in other symmetrical molecules whose nuclei have spin momentum, and it will also occur for deuterium, but we will confine this discussion to the case of hydrogen, since, apart from the case of deuterium, none of the other pairs of isomeric molecules exhibit any appreciable chemical differences.

Ortho and para hydrogen differ in their internal molecular energy, which is less in the symmetrical para form than in the ortho form. This difference in energy shows itself by alternations in intensity in the band spectrum of molecular hydrogen, which were first observed in 1924 by Mecke, and, indeed, led to the subsequent developments of the subject. The energy difference also leads to

¹ For a review of the physical basis of this subject, see *Orthohydrogen, Parahydrogen and Heavy Hydrogen*, by A. Farkas (Cambridge University Press, 1935).

a dependence of the relative proportions of the ortho and para forms on temperature. At the absolute zero hydrogen would consist of the pure para form, which has the lower internal energy, while as the temperature is raised the proportion of the ortho form would increase. It has been shown theoretically that at very high temperatures the limiting proportions of the two forms

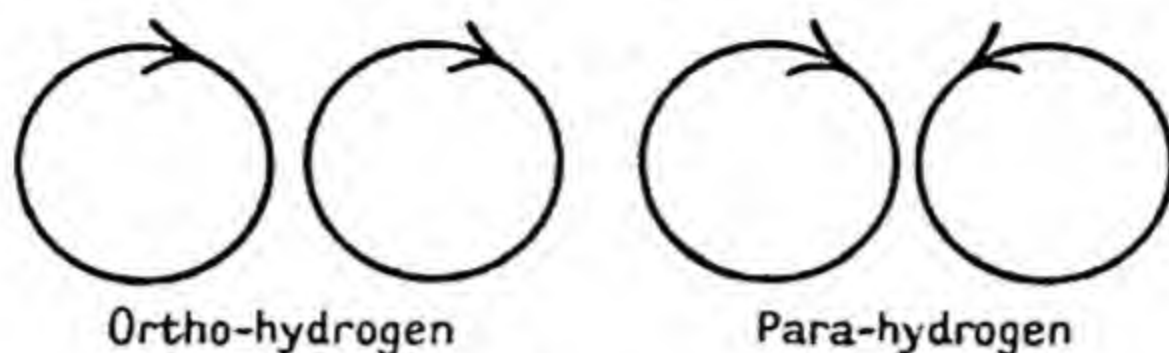


FIG. 45.

are three of ortho to one of para. The table below shows how the composition of the equilibrium mixture varies with temperature. The equilibria can be calculated theoretically, but have also been determined experimentally.

Table 1

<i>Temperature (Abs.)</i>	<i>% of para H₂</i>	<i>% of ortho H₂</i>
20°	99.82	0.18
40°	88.61	11.39
80°	48.39	51.61
120°	32.87	67.13
273°	25.13	74.87
∞	25.00	75.00

The thermal conductivities and specific heats of the two forms are different, and it is possible to utilize these properties in measuring the composition of a mixture. The change in the proportions of ortho and para hydrogen in the gas does not take place readily on altering the temperature unless some form of catalyst is used. Bonhoeffer and Harteck² showed from heat conductivity measurements at low pressures that equilibrium under some conditions was not reached in a year. By allowing ordinary hydrogen to be in contact with active carbon at 20° Abs., however, equilibrium was set up rapidly, and the gas which was pumped off consisted of para hydrogen of 99.7 per cent purity. This para hydrogen could be stored in glass vessels at room temperature for a week without appreciable conversion. The equilibrium mixture, with

² *Naturwiss.*, 1929, 17, 182.

approximately 25 per cent of para hydrogen, is obtained again by any one of the following means.

- (1) Treatment with metallic catalysts (*e.g.* Fe or Pt).
- (2) By passage through an electric discharge.
- (3) By admixture with atomic hydrogen.
- (4) By heating to temperatures of 800° or more.

It should be noted that enrichment with ortho hydrogen beyond the 3 : 1 equilibrium mixture ratio is not possible. Accordingly, it is not feasible to compare the physical properties of the two forms, although such a comparison between the para form and ordinary hydrogen can be made.

Para hydrogen and ordinary hydrogen have an appreciable difference in vapour pressure, as is shown by the data given below for temperatures of 13.95° Abs. and 20.39° Abs., which are the triple and boiling-points, respectively, of ordinary hydrogen.

Table 2

Temperature (Abs.)	Vapour pressure (mm.)	
	Normal hydrogen	Para hydrogen
13.95°	53.9	57.0
20.39°	760.0	787.0

The pure para form has a melting-point of 13.83° Abs. The magnetic properties of the two forms of hydrogen are also different. In para hydrogen the nuclear spins compensate one another and the magnetic moment of the molecule is zero, whereas in ortho hydrogen the spins act in conjunction and the moment, extrapolated from data for known ortho-para mixtures, is found to be approximate to twice the moment of a proton. It should be borne in mind, however, that this magnetism due to nuclear spin is much less than that arising from extra-nuclear factors.

The fact that the thermal conductivities and heat capacities of the two forms of hydrogen are different has already been mentioned. The utilization of these differences in analysing ortho-para mixtures has been developed by various workers, the type of apparatus used being shown in Fig. 46.

The conductivity cell, which is immersed in liquid air or liquid hydrogen, contains a fine wire, which is heated by a small battery of cells to 160 – 180° Abs., and forms one arm of a Wheatstone bridge. Its resistance is used as a measure of its temperature, the

latter being controlled by the thermal conductivity of the gas surrounding the wire. With a constant heating current and pressure, the wire will reach a higher temperature in normal hydrogen than in para hydrogen, because the latter has a higher thermal conductivity. Thus by first calibrating the cell with ordinary hydrogen and with pure para hydrogen it is possible, since there is a linear relationship between the conductivity and the para hydrogen content of the mixture, to analyse unknown mixtures of the two forms of hydrogen. There have been various modifi-

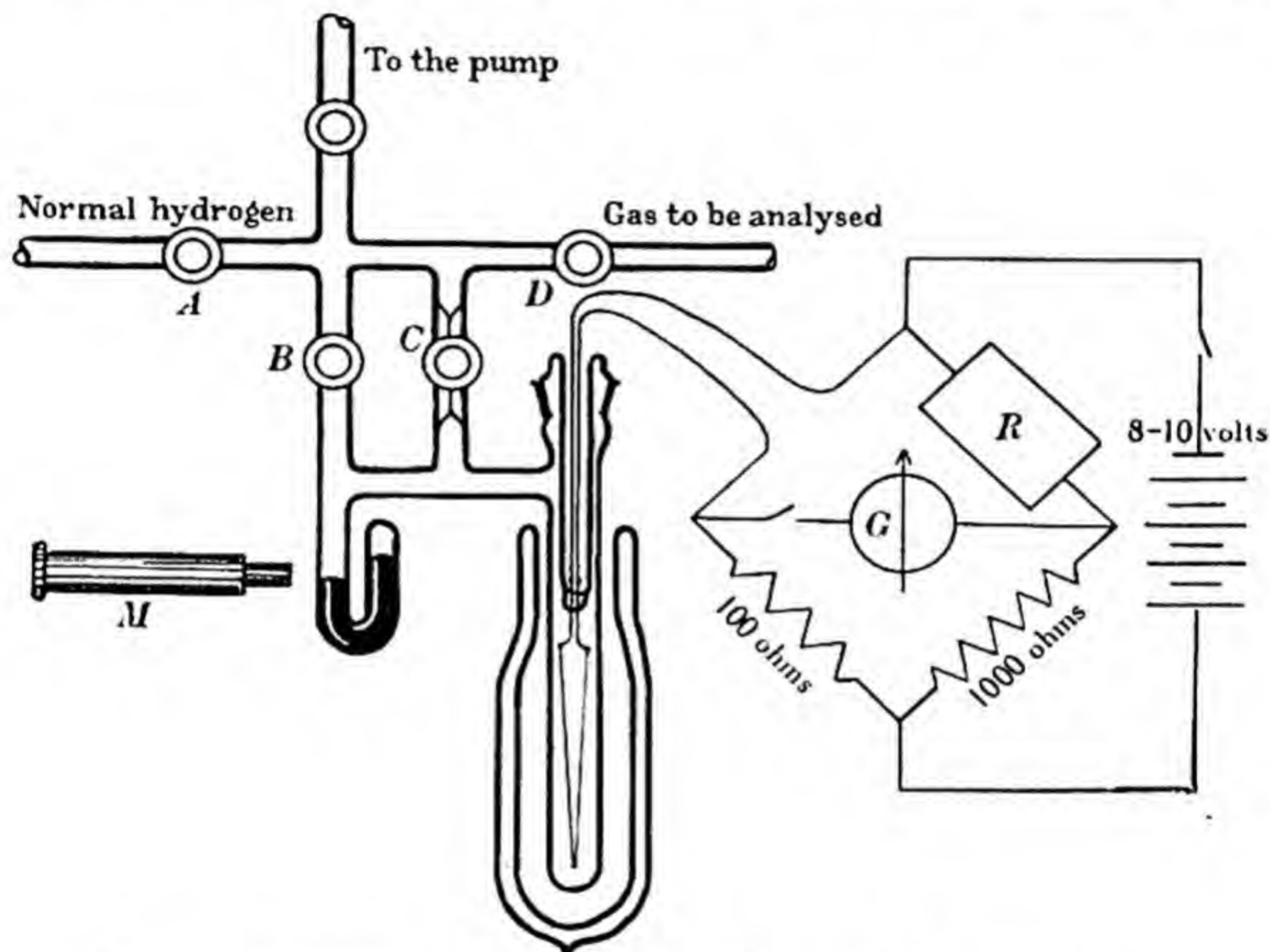


FIG. 46.—Apparatus for analysis of ortho-para hydrogen mixtures.
(From *Orthohydrogen, Parahydrogen, and Heavy Hydrogen*, by A. Farkas.)

cations of this method for application in special cases. Thus normally the measurements are made at a pressure of 20–40 mm., but A. Farkas³ has developed a method for operating with a cell of 2 c.c. capacity and gas pressures of 0.05 mm.

The catalytic properties of different materials in bringing about the ortho-para conversion have been extensively studied. The thermal conversion at 800–1000° is a homogeneous reaction, and is believed to be due to the production of hydrogen atoms by thermal dissociation of hydrogen. Certain paramagnetic substances

³ *Z. physikal. Chem.*, 1933, B, 22, 344.

have been found to catalyse the conversion. Thus oxygen, nitric oxide and nitrogen dioxide, all of which are paramagnetic, are effective (L. Farkas and Sachsse ⁴). Thanks to the development of reliable analytical methods, studies of this sort are quite readily carried out. Many diamagnetic gases, such as N_2 , N_2O , CO_2 , NH_3 , HI and SO_2 , were incapable of causing conversion. Paramagnetic ions in solution were also found to transform para hydrogen into the equilibrium mixture, the effect being greater the greater the magnetic moment of the ion in question. In the table below the velocity constants for the conversion by half-molar solutions of different ions are given, together with the magnetic moments of the ions in question.⁵

Table 3

Ion	Magnetic moment in magnetons	k in mole ⁻¹ litre min ⁻¹
Zn ⁺⁺ . .	0	0
Cu ⁺⁺ . .	1.9	1.15
Ni ⁺⁺ . .	3.2	1.95
Co ⁺⁺ . .	5.1	5.56
Fe ⁺⁺ . .	5.3	6.05
Mn ⁺⁺ . .	5.8	8.05

The heterogeneous conversion was first observed with charcoal as a catalyst. When ordinary hydrogen is passed through a tube packed with charcoal and cooled in liquid air, the equilibrium proportion of para hydrogen corresponding to the temperature of liquid air is found to be formed rapidly. Charcoal is not effective as a catalyst at ordinary temperatures. Platinum black, on the other hand, is a good catalyst at room temperature, but is not effective at the temperature of liquid air. The effect of temperature on the activity of different catalysts is rather complex. Sodium chloride has a minimum activity in the neighbourhood of room temperature, as has copper powder. Taylor and Diamond ⁶ have shown from a study of the catalytic activity of oxides at 86° Abs. (e.g. Cr_2O_3 , Gd_2O_3 , Nd_2O_3 , V_2O_3 , V_2O_5 , CeO_2 , ZnO , La_2O_3) that paramagnetic oxides are more active at this temperature. It has also been observed that certain substances are capable of poisoning catalysts for the ortho-para conversion.

⁴ *Ibid.*, 1933, B, 23, 1, 19.

⁵ Data from Farkas, *op. cit.*

⁶ *J. Amer. Chem. Soc.*, 1933, 55, 2613.

The conversion of para hydrogen to an equilibrium mixture by means of atomic hydrogen has been demonstrated directly by Geib and Harteck.⁷ Para hydrogen-rich hydrogen, prepared by desorption from charcoal cooled in liquid air or liquid hydrogen, was allowed to mix with hydrogen streaming away from a discharge tube and therefore carrying hydrogen atoms (*cf.* p. 306). Partial conversion to the equilibrium ortho-para mixture was observed, analyses being made by the method already outlined. By carrying out the reaction $p\text{-H}_2 + \text{H} = o\text{-H}_2 + \text{H}$ at various temperatures, the energy of activation of this process was found to be 7250 ± 250 g. cal. The fact that atomic hydrogen is able to bring about the conversion has been utilized in measuring the stationary concentration of hydrogen atoms in the photochemical reaction between hydrogen and chlorine.⁸ The same principle has been employed by Farkas and Harteck in determining the concentration of hydrogen atoms in the photochemical decomposition of gaseous ammonia by light of wave-length less than about 2000 Å. There are other grounds for supposing that the primary photochemical reaction in this instance is $\text{NH}_3 + h\nu = \text{NH}_2 + \text{H}$, but the fact that the system undergoing photolysis can actually bring about the ortho-para hydrogen conversion is proof that hydrogen atoms are present (unless, of course, it could be shown that radicals such as NH and NH_2 were able to produce the same effect as H). Cremer, Curry and Polanyi⁹ have used the same method for studying the relative reactivity of simple molecules (*e.g.* CCl_4 , CHCl_3 , CH_2Cl_2 , CH_3Cl) with atomic hydrogen.

Deuterium and its Compounds.

The existence of a heavy isotope of hydrogen was first suspected after the discovery of a discrepancy in atomic weight data. Aston's value for the atomic weight of hydrogen relative to the standard $\text{O} = 16.000$ was 1.00778 ± 0.00015 . This value, determined in 1927, was based on the application of the mass spectrograph and appeared to be in good agreement with the chemically determined value of 1.00780. In 1929, however, Giauque and Johnston showed from observations on the band spectrum of oxygen that the element was not simple, but had isotopes of mass 17 and 18. The atomic weight of oxygen, calculated from the relative abundance of these isotopes, was found to be 16.0035. If the chemical atomic weight of hydrogen is changed from the standard $\text{O} = 16.000$ to $\text{O} = 16.0035$,

⁷ *Z. physikal. Chem.*, 1931, *Bodenstein-Festband*, 849.

⁸ Geib and Harteck, *Z. physikal. Chem.*, 1931, B, 15, 116.

⁹ *Z. physikal. Chem.*, 1933, B, 23, 445.

a value of 1.00799 is obtained for hydrogen, which is definitely greater than Aston's physical value. The discrepancy would be accounted for on the assumption that ordinary hydrogen contained about 1 in 4500 of a heavier constituent of mass 2.¹⁰

This suggestion was rapidly put to the test and verified by observations on the optical spectrum of the residues left after evaporating liquid hydrogen, and also by application of the mass spectrograph, but from the point of view of the chemist a big problem remained, namely, how to prepare the new isotope of hydrogen in sufficient quantity for the study of its chemical reactions. Many methods were, of course, possible and practically all were tried. These included the fractional distillation of water with a view to separating D_2O from H_2O and HDO . The differences in boiling-point are known to be small, but an enrichment of the tail fractions in D_2O was actually observed by several workers. Distillation of other deuterium compounds (*e.g.* CH_4 - CD_4 mixtures) was also studied and gave positive results, as did the fractional freezing of ordinary water, and the fractional desorption of hydrogen from charcoal at liquid air temperatures. The hydrogen isotopes are also partially separated by diffusion through palladium, while by use of the Hertz diffusion apparatus (*cf.* p. 25) a small quantity of pure deuterium was isolated.

Almost without exception the above methods are laborious and the separation effected is small. The preparation of pure deuterium in quantity first became possible as the result of an observation made by Washburn and Urey,¹¹ that when water is electrolysed the residue becomes enriched in deuterium oxide. Various degrees of enrichment were observed in industrial electrolytic plant, irrespective of whether an acid or alkaline medium had been used in the electrolysis. Small enrichments have also been observed in water from various natural sources, but these can usually be explained readily in terms of preferential evaporation, preferential diffusion, or some such cause.

The enrichment of deuterium in water by electrolysis may be judged from the following figures, which refer to the electrolysis of caustic soda solution, made up with water from commercial electrolytic cells, between sheet nickel electrodes, with periodic distillation of the residues to free them from accumulated alkali. The figures in the last column show the volume of liquid put through each stage of the process. The gas evolved in the later stages of this electrolysis was burned and returned to the process, as it consisted of a deuterium-hydrogen mixture containing a considerable

¹⁰ Birge and Menzel, *Phys. Rev.*, 1931, 37, 1669.

¹¹ *Proc. Nat. Acad. Sci.*, 1932, 18, 496.

amount of deuterium. The data are taken from the work of Taylor, Eyring and Frost.¹²

Table 4

Stage of electrolysis	Density of product d_{40}^{20}	% hydrogen which is heavy	Volume electrolysed
1 . . .	0.998	—	610 gal.
2 . . .	0.999	0.5	90 gal.
3 . . .	1.001	2.5	52 l.
4 . . .	1.007	8	10.15 l.
5 . . .	1.031	30	2.00 l.
6 . . .	1.098	93	420 c.c.
7 . . .	1.104	99	82 c.c.

The electrolytic production of pure deuterium oxide is now carried out commercially. The densities of D_2O and H_2O differ by approximately 10 per cent, and density measurements therefore constitute a ready method of determining the constitution of a given sample. The density is not, however, a reliable guide as to composition unless it has been verified that no enrichment in the oxygen isotope has taken place in the electrolysis. This may be checked by 'normalizing' the water by treatment with successive quantities of ammonium chloride, which removes deuterium by an exchange reaction (*vide infra*), and determining if the density reverts to that of ordinary water.

Physical Properties of Deuterium and its Compounds.

Deuterium and its compounds differ appreciably in their physical properties from their hydrogen analogues. The melting-points, boiling-points and latent heats of fusion and evaporation of the molecules H_2 , HD and D_2 , which are tabulated below¹³ (Table 5), illustrate this point.

Table 5

	H_2	HD	D_2
M.p., °	— 259.2	— 256.5	— 254.5
B.p., °	— 252.7	—	— 249.5
Latent heat of fusion, g. cal.	28.0	37	47.0
Latent heat of evaporation, g. cal.	219.7	263	302.3

¹² *J. Chem. Phys.*, 1933, 1, 823.

¹³ Clusius, *Z. Elektrochem.*, 1938, 44, 15.

Among the compounds of deuterium similar differences exist, deuterium oxide being of special interest because it is the starting material for the preparation of most deuterium compounds. Like water, it is an associated liquid. The following table (Table 6) illustrates the differences in some of the chief physical properties of the two compounds.

Table 6

	H_2O	D_2O
Boiling-point	100°	101.4
Melting-point	0°	3.8°
Specific gravity 20°	0.9982	1.1059
Temp. of max. density	4.08°	11.22°
Heat of vaporization (cals./mole) . .	9700	9960
Dielectric const.	82	80.5
Viscosity at 20°	10.09	12.6
Refractive index	1.33300	1.32844
Surface tension (dynes/cm.)	72.75	67.8

Ionic mobilities in D_2O are less than in H_2O , but this effect may be accounted for by the greater viscosity. In most cases salts are somewhat less soluble and the heats of solvation of ions are smaller in deuterium oxide. Salt hydrates and deuterates also show small differences in dissociation pressures and in transition temperatures.

There are similar differences in melting- and boiling-point between many other deuterium compounds and their hydrogen analogues, though, as is shown by the few examples given below (Table 7), the values for the deuterium compounds are not always higher.

Table 7

Compound	<i>m.p.</i> °	<i>b.p.</i> °	Compound	<i>m.p.</i> °	<i>b.p.</i> °
NH_3 . .	− 77.8	− 33.3	CH_4 . .	− 182.6	
ND_3 . .	− 73.5	− 31.0	CD_4 . .	− 184.0	
H_2S . .	− 85.5		C_6H_6 . .	5.5	80.1
D_2S . .	− 86.0		C_6D_6 . .	6.6	79.2
HCl . .	− 110.9	− 85.0	HCN . .	− 14	25.3
DCl . .	− 114.9	− 81.5	DCN . .	− 12	25.9

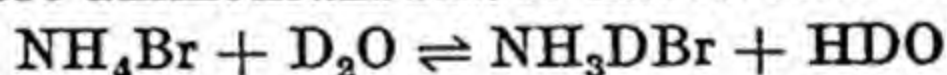
Preparation and Reactions of Deuterium Compounds.

Deuterium may be prepared from deuterium oxide by electrolysis, or by any other preparative method capable of yielding hydrogen. A great many deuterium compounds are also produced in reactions analogous to those used in preparing the corresponding hydrogen

compounds. For example, deuterium may be combined directly with the halogens, and deuterium oxide will react with acid anhydrides (*e.g.* SO_3 , P_2O_5) to form the deuterium acids. Similarly oxides such as Na_2O and CaO form NaOD and Ca(OD)_2 with deuterium oxide, and salt-like metallic sulphides, nitrides, phosphides and arsenides give the deuterium analogues of the corresponding hydrides on treatment with deuterium oxide or a deuterium acid. Many other examples of this sort could be quoted.

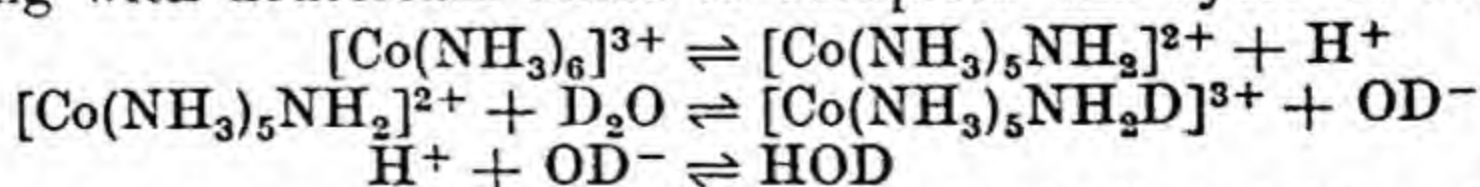
Exchange Reactions: A rather different approach to the preparation of deuterium compounds is by the exchange of hydrogen for deuterium under suitable experimental conditions. At high temperatures deuterium will react with H_2 to form HD , and will also exchange with part of the hydrogen in molecules such as NH_3 , OH_2 or CH_4 . These reactions often occur at lower temperatures on suitable hydrogenation catalysts such as palladium or nickel.

Exchange reactions also occur with great readiness in liquids which contain ions. If, for example, NaOH is dissolved in D_2O , there is a rapid ionic reaction and a mixture of NaOH and NaOD may be recovered from the solution. A similar, but less obvious, exchange occurs if an ammonium salt is dissolved in deuterium oxide (or a deuterio ammonium salt is dissolved in normal water), *e.g.*

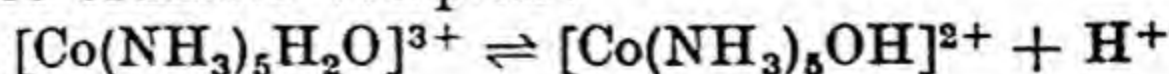


This reaction illustrates the dissociation of the ammonium ion in solution into H^+ and NH_3 , and also the equivalence of all four hydrogen atoms since, on treatment of the ammonium salt (NH_4X) with successive quantities of D_2O , the final product is ND_4X .

Deuterium exchange also occurs rapidly with amines (*e.g.* $\text{NH}_2\text{CH}_3\cdot\text{HCl}$) dissolved in water, and even with such compounds as hexammine cobaltic chloride, $(\text{Co}(\text{NH}_3)_6)\text{Cl}_3$, trisethylenediamine cobaltic chloride, $\text{Co}(\text{C}_2\text{H}_4(\text{NH}_2)_2)_3\text{Cl}_3$, or tetrammine platinous chloride, $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$, there is a slower reaction. The rate at which interchange occurs in deuterium oxide has been measured by precipitating the salt from solution by some suitable reagent after various intervals of time—*e.g.* precipitating tetrammine platinous chloride as Magnus' salt, $\text{Pt}(\text{NH}_3)_4\text{PtCl}_4$ —and determining the change of concentration. It is believed that the ammine cations undergo an acid dissociation to a very small degree, the dissociated form then reacting with deuterium oxide to complete the cycle of changes:



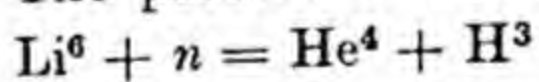
This mechanism parallels the known mode of dissociation of water within the co-ordinate complex:



For the deuteration of organic compounds¹⁴ various methods are available. Catalytic exchange reactions with deuterium itself have been mentioned already. Deuterium oxide addition to unsaturated compounds occurs exactly as in the case of water. Acetone will undergo an exchange reaction with deuterium oxide in alkaline solution, due, it is believed, to the reaction of the ketone in its enolic form, $\text{CH}_3\text{C}(\text{OH})=\text{CH}_2$. Nitromethane also reacts with deuterium oxide in presence of alkali, and here again it is believed to be the enolic form, $\text{CH}_2=\text{N}(\text{OH})\text{O}$, which is effective. The result of this exchange is the introduction of deuterium into the alkyl group, and by reduction of the final product (CD_3NO_2) to CD_3NH_2 , followed by further treatment with deuterium oxide, the fully deuterated compound, CD_3ND_2 , may be obtained. These examples, taken at random from the very extensive literature of the subject, serve to illustrate the importance of exchange reactions in this field.

Tritium.

Tritium (H^3 or T), the radioactive isotope of hydrogen of mass 3.0169, was discovered in 1934 by Oliphant, Harteck and Rutherford¹⁵ as a product of the bombardment of deuterium compounds such as D_3PO_4 and $(\text{ND}_4)_2\text{SO}_4$, with deuterons. The nuclear reaction which occurs is $d + d = t + p$. There are now several other methods for preparing the new isotope, the most convenient of which is the irradiation of lithium or a lithium compound with slow neutrons derived either from a nuclear reactor (see p. 535) or a cyclotron reaction. The process which occurs is:



The tritium produced may be separated from helium by absorption in uranium metal, with which it forms the compound UH^3_3 , and regenerated subsequently by heating to 500° . Alternatively it may be oxidized to $(\text{H}^3)_2\text{O}$ and isolated in this form. Another convenient source for small amounts of tritium is beryllium which has been bombarded in the cyclotron with deuterons for the production of neutrons ($\text{Be}^9(d,n)\text{B}^{10}$). In this case it is formed in the secondary reaction $\text{Be}^9 + d = 2\text{He}^4 + \text{H}^3$. Part of the tritium formed is liberated as gas during the bombardment: that remaining in the metal may be driven off by heating in vacuum and then oxidized. The primary product in all these reactions is the tritium nucleus, or triton, which, however, readily gains electrons under the experimental conditions used and forms neutral tritium atoms and

¹⁴ For a more detailed review of this topic, see Sidgwick, *The Chemical Elements and their Compounds* (Clarendon Press, Oxford, 1950), Vol. I, p. 52.

¹⁵ *Nature*, 1934, 133, 412.

molecules. Tritons are formed in various other nuclear reactions (e.g. $C^{12}(n,t)B^{10}$; $N^{14}(d,t)N^{13}$; $Cu^{63}(d,t)Cu^{62}$).

Tritium decays by emission of β -particles of low energy (max. 18.3 ± 0.2 K.e.v.; mean 5.69 ± 0.06 K.e.v.) and has a half-life of $12.46 \pm 0.2y$. The decay product is the helium isotope He^3 . The low energy of the β -particles introduces a measure of difficulty into its detection by the Geiger-Mueller counter, as the rays will not penetrate the counter window. The tritium must therefore be introduced as gas into the interior of the counter, or, alternatively the light pulses produced when the β -particles impinge on a film of naphthalene may be recorded with a photomultiplier tube. The short life of tritium precludes its occurrence in nature, and early reports of its detection were shown by Aston to be due to confusion in mass-spectrographic observations between lines due to the ions $(D_2H)^+$ and $(DT)^+$.

The purely chemical work so far done with tritium is very limited. The equilibrium $HT + H_2O = H_2 + HTO$ has been studied.¹⁶ The differences in physical properties between hydrogen and tritium are likely to be greater than in the case of hydrogen and deuterium, and the same will be true of their respective compounds, though very few have been described. The main application of tritium in chemistry is likely to be as a tracer.¹⁷ Reference has been made already to the use of deuterium in this way. The assay of the deuterium content of compounds depends on the mass spectrograph, density determinations or some such method. In the case of tritium β -ray counts are used directly for assay in the study of exchange reactions and of the behaviour of tritium-labelled groups in organic molecules. It is possible by using the radioactivity of tritium to measure accurately much smaller quantities than in the case of deuterium.

The Hydrides.

The compounds of the elements with hydrogen fall into three fairly distinct classes, namely, the volatile, the salt-like, and the interstitial hydrides. Those in the first class have covalent bonds, and include derivatives of the following elements:

Group	III	IV	V	VI	VII
	B	C	N	O	F
	[Al]	Si	P	S	Cl
	Ga	Ge	As	Se	Br
	[In]	Sn	Sb	Te	I
		Pb	Bi	Po	

¹⁶ Black and Taylor, *J. Chem. Phys.*, 1943, 11, 395.

¹⁷ See Kamen, *Radioactive Tracers in Biology* (Academic Press Inc., New York, 1947).

In the second class are the hydrides of the alkali and alkaline earth metals, and possibly also those of lanthanum, cerium, praseodymium and neodymium. These are solids with ionic lattices. The last group includes the hydrides of elements such as titanium, zirconium, vanadium and uranium. It should be added that the distinction between salt-like and interstitial hydrides is not always clear. Several cases where this uncertainty exists are referred to below.

The Boron Hydrides.

The formation of hydrides of boron by the action of acids on magnesium boride has been known for about seventy years, but the isolation and study of the separate hydrides became possible only when special manipulative methods were developed by Stock and his co-workers.¹⁸ The difficulties in working with these compounds are due to their volatility and sensitivity to air, moisture and tap grease.

The melting- and boiling-points of the boron hydrides known at the present time are summarized in the table below. There are, in addition, a number of less well-defined solid hydrides, which are described in a later section.

Table 8

<i>Hydride</i>	<i>m.p.</i> °	<i>b.p.</i> °
B ₂ H ₆	— 165.5	— 92.5
B ₄ H ₁₀	— 120	18
B ₅ H ₉	— 46.6	48
B ₅ H ₁₁	— 123	63
B ₆ H ₁₀	— 65	v.p. at 0°, 7.2 mm.
B ₁₀ H ₁₄	99.7	213

Three main methods are available for preparing these substances,¹⁹ namely :

- (1) The reaction of magnesium boride with aqueous acids.
- (2) The reaction of boron trichloride or tribromide with hydrogen in the electrical discharge, followed by decomposition of the halogen derivative (B₂H₅Cl or B₂H₅Br) produced.
- (3) The reduction of a boron halide with lithium aluminium hydride.

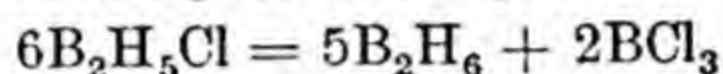
The third of these methods, which yields diborane, is now in general

¹⁸ Stock's work in this field is summarized in his monograph *The Hydrides of Boron and Silicon* (Cornell University Press, 1933). This book also discusses fully the special techniques employed.

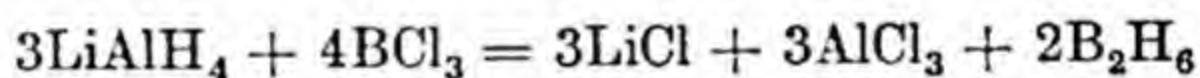
¹⁹ For review articles and bibliography, see Bell and Emeléus, *Quart. Rev. Chem. Soc.*, 1948, 2, 132; Schlesinger and Burg, *Chem. Rev.*, 1942, 31, 1.

use and has supplanted the other two. The decomposition of magnesium boride by acids (HCl or H_3PO_4) gives a rather low yield of tetraborane, B_4H_{10} , as the main product, together with small amounts of B_5H_9 , B_6H_{10} , $\text{B}_{10}\text{H}_{14}$, CO_2 , PH_3 and silicon hydrides. The last three are derived from impurities. It does not yield any diborane, B_2H_6 , probably because this substance is very rapidly decomposed by water or aqueous acids.

The second method, which was developed by Burg and Schlesinger, entails pumping a mixture of boron trichloride or tribromide and hydrogen at a pressure of 5–10 mm. through an electrical discharge between water-cooled copper electrodes. The issuing gas contains H_2 , HCl (or HBr), a little B_2H_6 , BCl_3 (or BBr_3), and $\text{B}_2\text{H}_5\text{Cl}$ (or $\text{B}_2\text{H}_5\text{Br}$). It is condensed in a U-tube cooled in liquid air, the hydrogen halide and B_2H_6 are distilled off at -120° and the residue of BCl_3 (or BBr_3) and $\text{B}_2\text{H}_5\text{Cl}$ (or $\text{B}_2\text{H}_5\text{Br}$) is kept at 0° , when it disproportionates according to the equation



The preparation of diborane by reducing boron trichloride with lithium aluminium hydride (*see* p. 281) gives an almost theoretical yield :



The lithium aluminium hydride is dissolved in ether, cooled, and a solution of boron trichloride in ether is added slowly with a stream of dry nitrogen passing through the reaction flask. A cold-finger reflux containing a solid carbon dioxide refrigerant prevents excessive loss of ether with the exit gas, from which diborane is condensed by passage through a U-tube cooled in liquid nitrogen. Boron trifluoride reacts similarly.

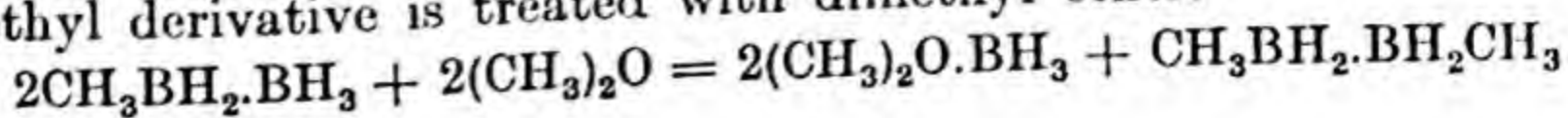
Interconversion of the Boron Hydrides.—The interconversion of the boron hydrides, and particularly the preparation of the higher hydrides from the readily accessible diborane, has assumed a special importance since the discovery of the lithium aluminium hydride method for preparing diborane. There appears to be a complex set of equilibria between the various hydrides, controlled by temperature and the presence of added hydrogen.^{19a} When, for example, diborane is passed through a tube heated to 100 – 120° , B_4H_{10} and B_5H_{11} are the main products. The hydride B_4H_{10} , on the other hand, gives moderate yields of B_2H_6 when heated at about the same temperature, while in the thermal decomposition of B_5H_{11} at 100° , H_2 , B_2H_6 , B_4H_{10} , B_5H_9 and $\text{B}_{10}\text{H}_{14}$ are all formed. In this case the yield of B_2H_6 and B_4H_{10} is enhanced by the addition of a large excess of hydrogen.

^{19a} *See, for example, Clarke and Pease, J. Amer. Chem. Soc., 1951, 73, 2132.*

Non-Volatile Boron Hydrides.—No volatile boron hydrides other than those given in the table are known, but several non-volatile solid hydrides have been produced by the action of heat on the volatile compounds. Thus diborane, on heating in a glass vessel at 120° , gives a colourless film of a hydride of the approximate formula $[\text{BH}_{1.5}]_x$, which is insoluble in carbon disulphide. On further heating this is transformed into a yellow insoluble material. B_4H_{10} on heating gives a yellow insoluble hydride, together with a colourless solid hydride which is soluble in carbon disulphide and which has a molecular weight of about 140 ($\equiv \text{B}_{12}$). Spontaneous decomposition of B_6H_{10} at room temperature gives a yellow crystalline hydride, which, from cryoscopic measurements in benzene, has the formula $\text{B}_{26}\text{H}_{36}$. Little is known, however, about the relationship between these various solid hydrides, and it is evident that they merit further study.

General Properties of the Boron Hydrides.—Certain reactions are common to all the boron hydrides. Thus they are decomposed into boron and hydrogen at a red heat, and the pyrolysis of diborane is used to prepare pure boron. They explode with oxygen on heating or sparking, forming, if excess oxygen is present, boron trioxide and water. There is evidence that some of the higher hydrides are spontaneously inflammable. All are hydrolysed by water, B_2H_6 very rapidly ($\text{B}_2\text{H}_6 + 6\text{H}_2\text{O} = 2\text{H}_3\text{BO}_3 + 6\text{H}_2$), B_4H_{10} and B_5H_{11} moderately rapidly and B_6H_9 , B_6H_{10} and $\text{B}_{10}\text{H}_{14}$ only very slowly. Hydrolysis with aqueous alkali occurs readily for all and is convenient as an analytical method, since each boron-hydrogen bond in the molecule yields one molecule of hydrogen. All of the hydrides react with the halogens, forming various substitution products. Diborane reacts with halogen halides in presence of the corresponding aluminium halide, forming the mono-halogenated product (e.g. $\text{B}_2\text{H}_6\text{Cl}$) and hydrogen. The other hydrides would probably react similarly.

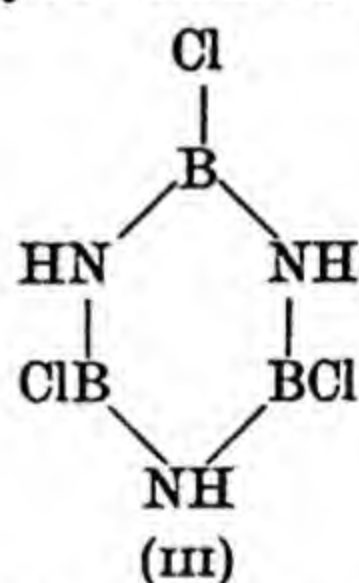
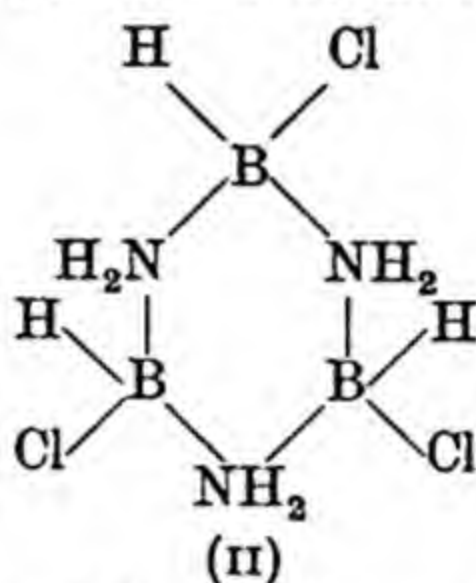
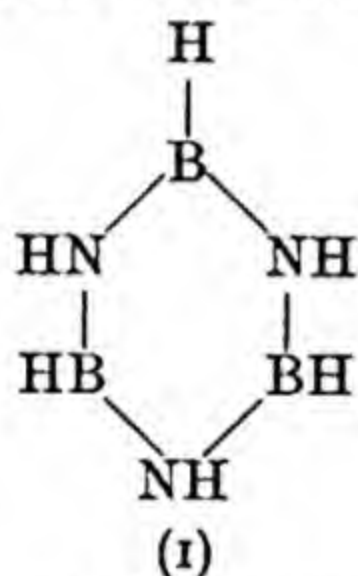
Methyl derivatives of diborane are formed in its reaction with boron trimethyl, which is reversible. Other boron alkyls react with diborane similarly, but this method has not yet been applied in preparing alkyl derivatives of other boron hydrides, nor have the reactions with other organometallic compounds been investigated. In the methylation of diborane the products are $\text{CH}_3\text{.BH}_2\text{.BH}_3$, $(\text{CH}_3)_2\text{BH.BH}_3$, $(\text{CH}_3)_2\text{BH.BH}_2(\text{CH}_3)$ and $(\text{CH}_3)_2\text{BH.BH}(\text{CH}_3)_2$, as may be proved by characterizing the methyl boric acids formed on hydrolysis. The symmetrical compound $\text{CH}_3\text{.BH}_2\text{.BH}_2\text{CH}_3$ is not formed by direct alkylation, but is obtained when the mono-methyl derivative is treated with dimethyl ether.



The remarkable fact that not more than four hydrogen atoms in diborane can be replaced by alkyl groups without rupture of the B—B bond and formation of the boron trialkyl is a strong argument for the bridge structure of diborane and is discussed later.

Reaction of Diborane with Ammonia.—The ammoniate of diborane, $B_2H_6 \cdot 2NH_3$, which is best formed when the two substances react at -120° , is a white solid which gives a conducting solution in liquid ammonia. When this solution is allowed to react with sodium at -77° , one g. mol. reacts with one equivalent of sodium and liberates one equivalent of hydrogen. The product is the salt $NaB_2H_6NH_2$. This is taken as evidence that the compound formed from ammonia and diborane contains one NH_4 ion per molecule and the formula is now written as $NH_4^+(H_3B \cdot NH_2 \cdot BH_3)^-$.

The ammoniates of B_2H_6 , B_4H_{10} and B_5H_9 lose hydrogen when heated in vacuum at 200° and borazole, $B_3N_3H_6$ (b.p. 55°), is formed. The same compound is obtained when diborane and ammonia are heated together. It is remarkably stable and has been shown by electron diffraction measurements to have the cyclic structure (I).

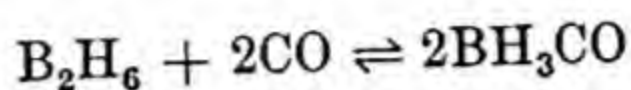


Borazole reacts in the cold with three molecular proportions of HCl, HBr, H_2O or CH_3OH as if it were unsaturated, and gives addition products of which the chloride (II) is typical. When the chloride is heated it loses hydrogen and forms the compound (III).²⁰ Methyl-substituted diboranes (*vide supra*) also form diammoniates which, when heated to $180-200^\circ$, give aminodimethyl borine ($B(NH_2)(CH_3)_2$), $B_3N_3H_6$, and the three methyl-substituted borazoles, $CH_3B_3N_3H_5$, $(CH_3)_2B_3N_3H_4$ and $(CH_3)_3B_3N_3H_3$. In these the methyl groups are attached to boron. They may also be formed by heating methyl boranes with ammonia. Borazoles with methyl groups attached to nitrogen atoms are formed when B_2H_6 , NH_3 and CH_3NH_2 are heated to 200° . Phosphine and diborane react to form the compound $B_2H_6 \cdot 2PH_3$, but there is as yet no evidence that this gives a phosphorus analogue of borazole on heating.

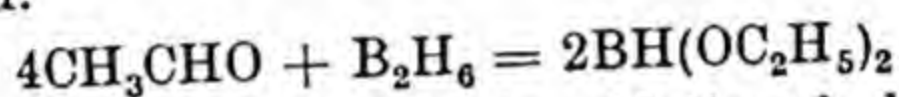
Derivatives of the Borine Radical.—The density of diborane gives

²⁰ Stock, Wiberg and Martini, *Ber.*, 1930, 63, 2927; Wiberg and Bolz, *Ber.*, 1940, 73, 209.

no indication of its dissociation into BH_3 radicals. Diborane does, nevertheless, form derivatives of this radical in a number of its reactions. With trimethylamine, for example, the stable co-ordination compound $\text{H}_3\text{B} \leftarrow \text{N}(\text{CH}_3)_3$ (b.p. 171°) is formed, in which the acceptor properties of boron are apparent. A similar reaction occurs between trimethylamine and alkylated diboranes. Diborane also reacts with carbon monoxide forming borine carbonyl (b.p. -64°)



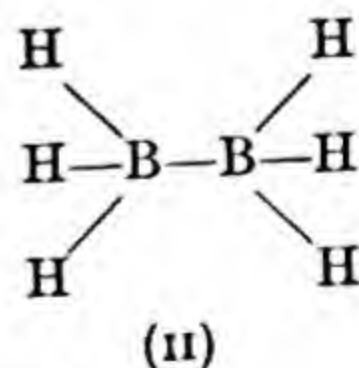
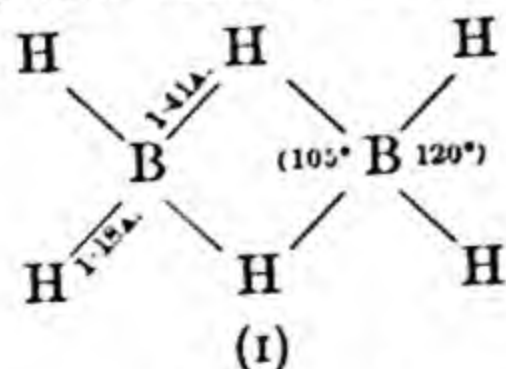
This is largely dissociated at 100° and reacts with trimethylamine at room temperature, forming CO and $\text{BH}_3\text{N}(\text{CH}_3)_3$. A co-ordination product of low stability, $\text{H}_3\text{B} \leftarrow \text{O}(\text{CH}_3)_2$, is formed by diborane and dimethyl ether. Substitution derivatives of the borine radical are also known. Thus in the reaction with acetaldehyde, diethoxyborine is formed.



A further example is afforded by N-dimethyl amino borine, $(\text{CH}_3)_2\text{NBH}_2$, which is obtained in the reaction of diborane with dimethylamine. The role of the borine radical in the interconversion of the boron hydrides is not yet fully understood. It is, however, extremely likely that it plays a part in these reactions and also in such reactions as the polymerization of acetylene and ethylene, which occur in presence of diborane.

Structure of the Boron Hydrides.—The boron hydrides are all electron deficient, i.e. they have too few valency electrons to form the minimum number of two-electron bonds needed. In diborane, for example, there are only twelve electrons available for bond formation, six provided by the two boron atoms and six by the hydrogen atoms, but fourteen are needed to satisfy the valency concept of two electrons per covalent bond.

It is now generally agreed that diborane has a structure of the type (I) in which two hydrogen atoms form a bridge between the boron atoms, with the electron deficiency occurring in the bridge, and not the ethane-like structure (II).

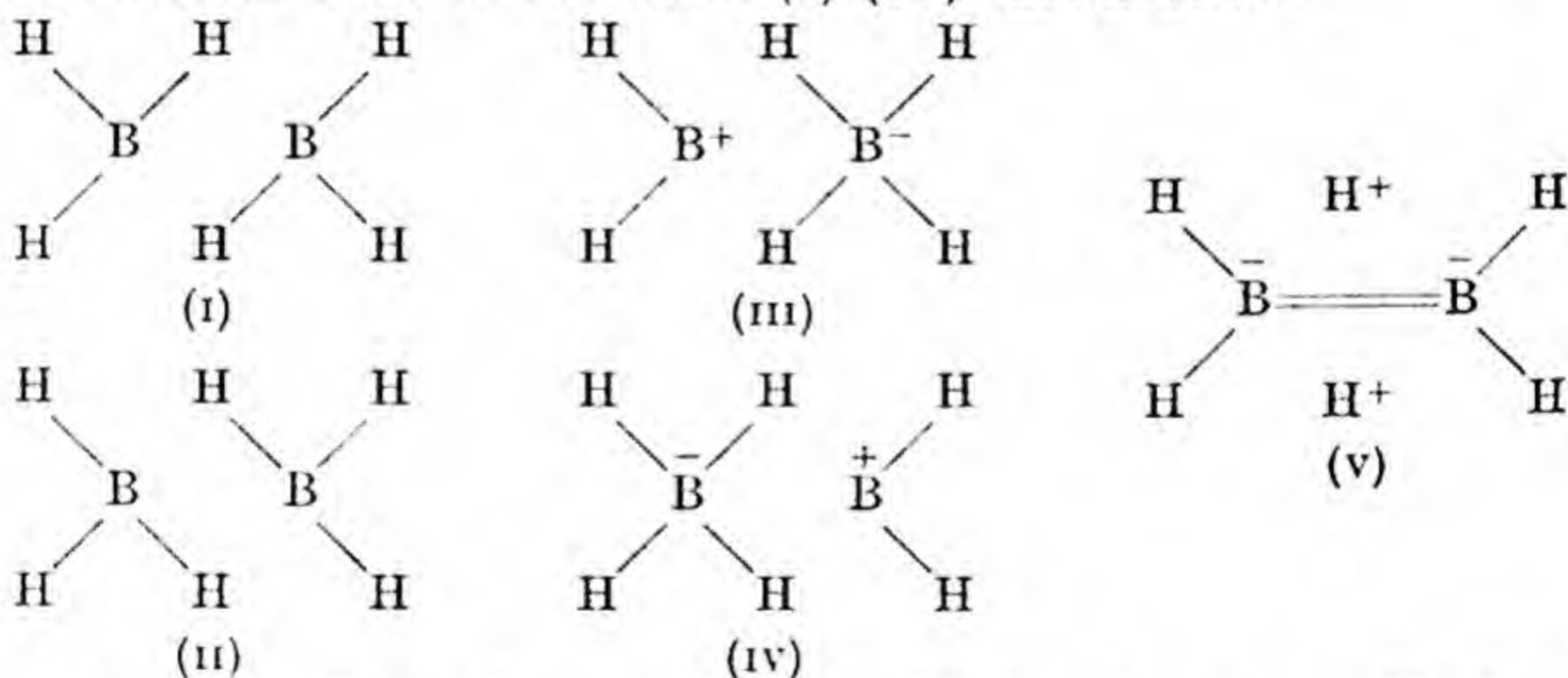


The only convincing chemical evidence for a bridge structure is the fact that not more than four hydrogen atoms (two attached to each boron atom) can be replaced by alkyl groups without rupture of the

B—B bond. Any attempt to introduce more than four methyl groups into the diborane molecule leads to boron trimethyl. Two hydrogen atoms are clearly different from the rest and are concerned with holding the molecule together.

Electron diffraction measurements on diborane were originally interpreted in terms of an ethane-like structure, but are equally consistent with a bridge structure having the dimensions shown above. Studies of the Raman spectrum of liquid diborane ²¹ and of the infra-red spectrum of the gas ²² also support the bridge structure. Major differences would be expected in the spectra of structures (I) and (II), and the observed results can only be accounted for by a bridge structure which, from the point of view of its characteristic frequencies, has much in common with ethylene. Low temperature specific heat measurements ²³ also indicate hindered rotation about the B—B bond.

The electronic structure of diborane was at one time represented either as ionic [$H_2^{++}B_2H_4^{--}$] or by formulæ with one-electron linkages. Both of these satisfy the difficulties of electron deficiency, but the physical properties of diborane are not those of an ionic molecule, and the liquid is a non-conductor. The presence of one-electron bonds would also lead to paramagnetism, whereas diborane is diamagnetic. The bridge structure is one in which resonance could occur between the forms (I)–(IV) shown below.²⁴



An alternative is the protonated double-bond structure (V), first suggested by Pitzer,²⁵ in which two protons are embedded in the

²¹ Anderson and Burg, *J. Chem. Phys.*, 1938, 6, 586.

²² Stitt, *J. Chem. Phys.*, 1941, 9, 780; Price, *ibid.*, 1947, 15, 614; Bell and Longuet-Higgins, *Proc. Roy. Soc.*, 1945, 183, A, 357.

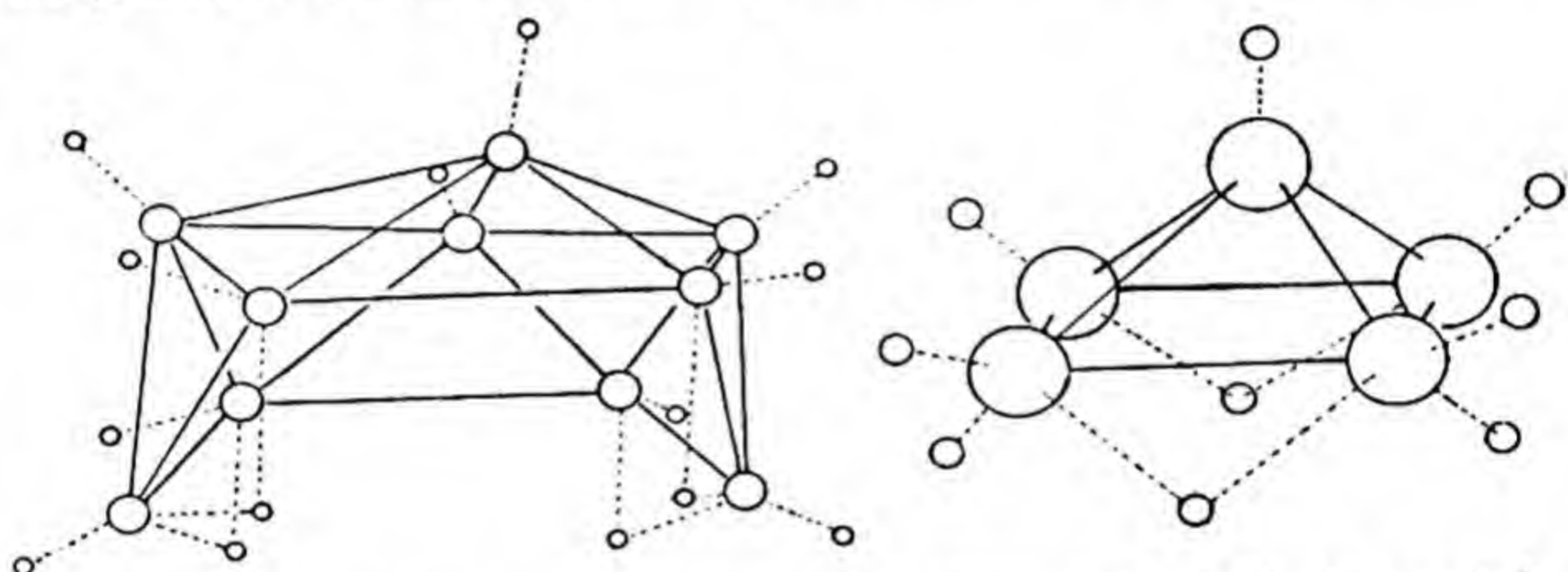
²³ Stitt, *J. Chem. Phys.*, 1940, 8, 981.

²⁴ For a more detailed discussion, see Bell and Emeléus, *Quart. Rev. Chem. Soc.*, 1948, 2, 132.

²⁵ *J. Amer. Chem. Soc.*, 1945, 67, 1126. See also Wiberg, *FLAT Review of German Science, Inorganic Chemistry, Part I*, 1948, p. 127.

π -electrons of the double bond, which are spread out at right angles to the plane of the rest of the molecule.

The structures of the remaining boron hydrides are very uncertain. The relationship between B_2H_6 and B_4H_{10} is shown by the synthesis of the latter from B_2H_5I and sodium. Apart from this, there is no chemical evidence. It is not even known how many alkyl groups can be substituted in these hydrides without breakdown of the parent molecule, though this would be the most direct way of finding the number of hydrogen bridges present. Pitzer has suggested formulæ for all the hydrides based on the combination, through hydrogen bridges, of hypothetical borine radicals such as BH_3 , $BH_2.BH_2$ and $BH_2.BH.BH_2$, but these are purely speculative.



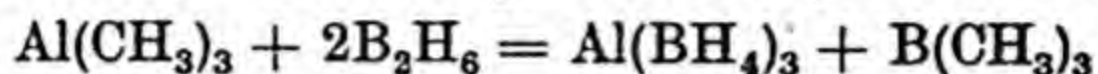
Recent X-ray determinations of the structures of single crystals of B_5H_9 and $B_{10}H_{14}$ give the first direct information on the molecules of the higher hydrides.^{25a} The boron atoms in pentaborane form a tetragonal pyramid, below the base of which are four hydrogen atoms, each bonded to two atoms of boron. The remaining five atoms of hydrogen are joined to single boron atoms, as shown above. The boron atoms in decaborane form two regular pentagonal pyramids with an edge in common. Ten hydrogen atoms are attached to single boron atoms and four form bridges. An important feature of this work is the fact that the positions of the hydrogen atoms can be determined from the electron density maps. It will doubtless be extended to the other hydrides. One may expect, moreover, that structural determinations by means of neutron diffraction will provide further confirmation of the molecular configurations. Methods are now being developed whereby the diffraction of a neutron beam may be made to yield information on structural parameters, and the method has the advantage that it enables the location of light atoms such as hydrogen and

^{25a} Dulmage and Lipscomb, *J. Amer. Chem. Soc.*, 1951, 73, 3539; Kasper, Lucht and Harker, *Acta Cryst.*, 1950, 3, 436.

deuterium to be found with greater certainty than in the approach based on X-ray or electron diffraction. The results of electron diffraction studies with pentaborane are stated to be consistent with the above structure.

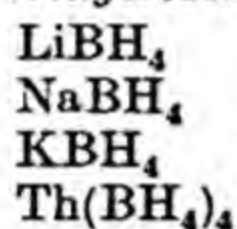
The Borohydrides.

A number of compounds are now known which contain the BH_4 group attached to a metal. The borohydrides so far prepared include the Li, K, Na, Be, Ca, Mg, Al, Ga, Ti, Zr, Hf, Th and U compounds. The first to be isolated was aluminium borohydride,²⁶ $\text{Al}(\text{BH}_4)_3$, which is formed by the reaction of aluminium methyl with diborane at 80° and is spontaneously inflammable.

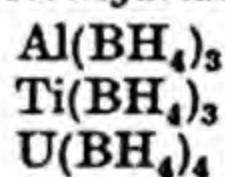


The borohydrides fall into two fairly distinct groups, some being ionic and some covalent in character. The following are examples :

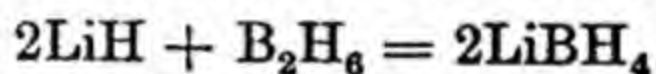
*Ionic
borohydrides*



*Covalent volatile
borohydrides*



The reaction of a metal alkyl with diborane is a general preparative method. Under suitable conditions borohydrides are also formed in the reaction between diborane and a metal hydride, *e.g.*



The borohydrides of lithium and of sodium have respectively orthorhombic and face-centred cubic lattices in which the $(\text{BH}_4)^-$ ion occurs as a unit. The lithium compound is stable in dry air but is rapidly hydrolysed by cold water. The sodium compound may be recrystallized from cold water, and can form a dihydrate. It is, however, decomposed by hot water. It is insoluble in ether and dioxane, but can be used as a reducing agent in aqueous solution, *e.g.* for sugars, for which lithium aluminium hydride is unsuitable. Sodium borohydride is a milder reducing agent than the lithium compound.

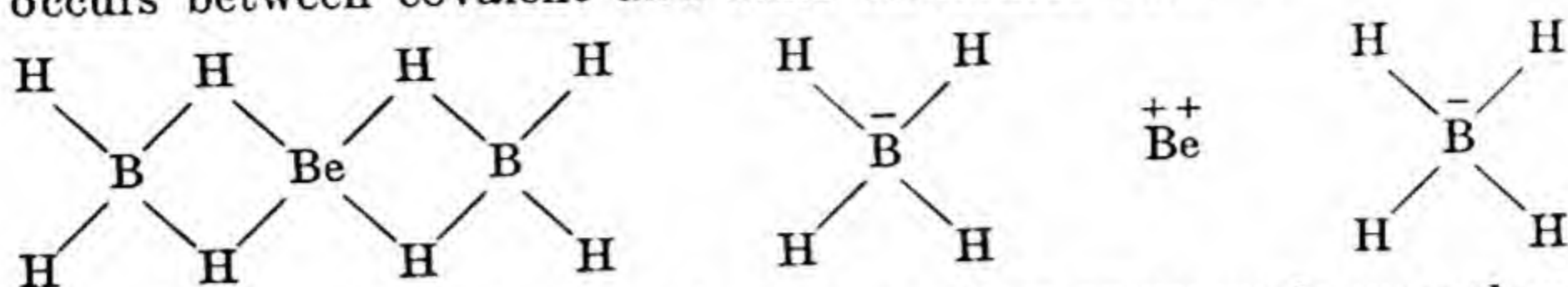
The compounds which Stock obtained by the reaction of sodium and potassium amalgams with diborane, and to which he ascribed the formulæ $\text{Na}_2\text{B}_2\text{H}_6$ and $\text{K}_2\text{B}_2\text{H}_6$, have recently been shown to have X-ray patterns identical with NaBH_4 and KBH_4 .²⁷ It is very probable, therefore, that the earlier work was in error.

The covalent borohydrides probably contain hydrogen bridges.

²⁶ Schlesinger, Sanderson and Burg, *J. Amer. Chem. Soc.*, 1939, 61, 536.

²⁷ Kasper, McCarty and Newkirk, *ibid.*, 1949, 71, 2583.

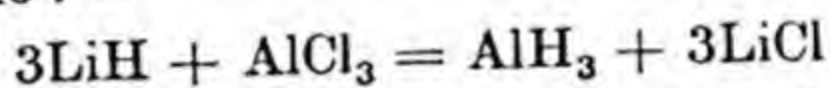
In beryllium borohydride, for example, it is thought that resonance occurs between covalent and ionic structures such as



The variation in ionic character among these compounds may then be explained by a greater or less contribution to the resonance by the ionic form.

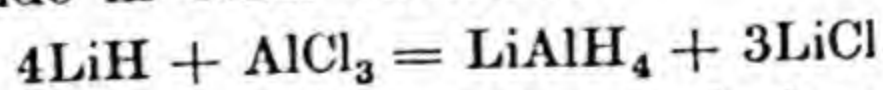
Hydrides of Aluminium, Gallium and Indium.

The electron deficiency which occurs in the boron hydrides should be found in hydrides of other Group IIIA elements, and this lends a special interest to these compounds. Aluminium hydride, AlH_3 , is known only as a non-volatile solid polymer, or in ether solution. It is formed when lithium hydride reacts with an ether solution of aluminium chloride: ²⁸



The aluminium hydride formed remains in solution initially, but gradually a white solid $(\text{AlH}_3)_x$ is deposited, from which ether cannot be removed completely without decomposition. A solid hydride of the same composition has also been described by Stecher and Wiberg.²⁹ When aluminium trimethyl mixed with a large excess of hydrogen is passed through a glow discharge, the products include dimeric compounds of the type $\text{Al}_2(\text{CH}_3)_{6-m}\text{H}_m$ and a solid $(\text{AlH}_3)_x$. The hydrides $(\text{AlH}_3)_x$ formed by these two methods are probably identical. The compound is stable in vacuum up to 100° , above which temperature decomposition to Al and H_2 occurs. The hydride reacts with diborane to form $\text{Al}(\text{BH}_4)_3$, and probably also $\text{AlH}(\text{BH}_4)_2$ and $\text{AlH}_2(\text{BH}_4)$. The structure of the solid aluminium hydride is unknown, but it is likely that it contains aluminium atoms joined by hydrogen bridges, as in diborane.

Lithium aluminium hydride, LiAlH_4 , the analogue of the borohydrides, is formed in the reaction between lithium hydride and aluminium chloride in ether solution.

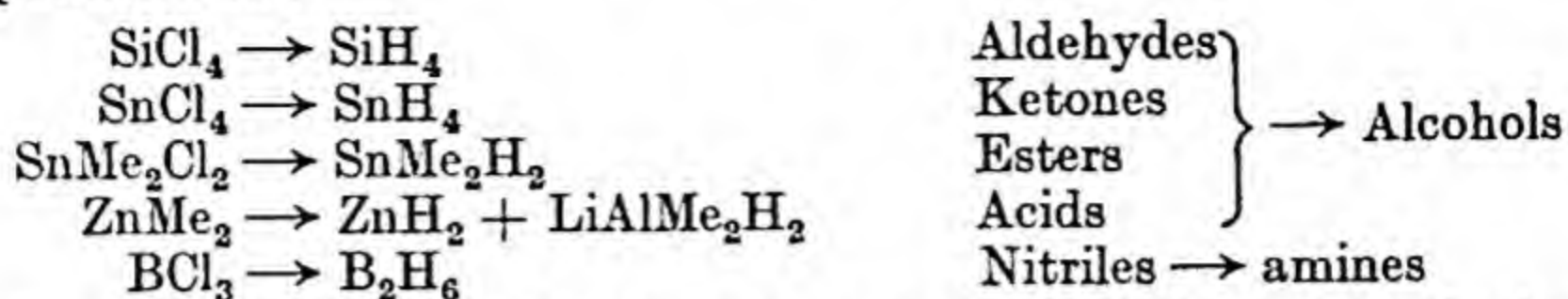


It is a white solid, which is readily hydrolysed by water with evolution of hydrogen. It is moderately soluble in ether (29 g./100 g.) and in this medium has proved a most valuable

²⁸ Finholt, Bond and Schlesinger, *J. Amer. Chem. Soc.*, 1947, 69, 1199.

²⁹ *Ber.*, 1942, 75, 2003.

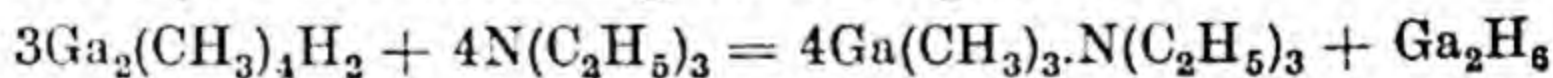
reducing agent. Typical reactions with inorganic and organic compounds are :



The great advantage of lithium aluminium hydride as a reducing agent for organic compounds is that it does not reduce olefinic double bonds unless they are substituted on the one side by a phenyl group and on the other by a reducible group (*e.g.* $-\text{C}=\text{O}$, $-\text{NO}_2$).

Other compounds of this type (*e.g.* NaAlH_4 , $\text{Ca}(\text{AlH}_4)_2$, $\text{Ti}(\text{AlH}_4)_4$, $\text{Sn}(\text{AlH}_4)_4$, $\text{In}(\text{AlH}_4)_3$, $\text{TlCl}(\text{AlH}_4)_2$) may also be prepared. They are not all stable, however, and the tin compound, for example, decomposes above -40° into aluminium hydride, tin hydride, and the decomposition products of the latter.^{29a} The titanium compound likewise decomposes at room temperature to titanium, aluminium and hydrogen: it is formed, like the tin compound, by reaction of the metal halide with lithium aluminium hydride in ether solution.^{29b} It has also been shown^{29c} that aluminium hydride readily forms a liquid compound $\text{AlH}_3 \cdot \text{AlCl}_3$ with aluminium chloride. This has a reactivity similar to that of LiAlH_4 , but has the advantage in the preparation from metal halides of hydrides which are insoluble in ether that the product is not contaminated with lithium salts.

Gallium forms a well-defined hydride, Ga_2H_6 .³⁰ Gallium trimethyl and hydrogen are passed through an electric discharge and yield a mixture of solid and liquid products from which tetramethyldigallane, $\text{Ga}_2(\text{CH}_3)_4\text{H}_2$, may be isolated. This reacts quantitatively with triethylamine according to the equation



The hydride has an extrapolated boiling-point of 139° , but decomposes above 130° into gallium and hydrogen. There can be little doubt that the structure is analogous to that of diborane and that many of its reactions will prove to be similar. Gallium also forms compounds analogous to lithium aluminium hydride (*e.g.* LiGaH_4 , $\text{Tl}(\text{GaH}_4)_3$).^{30a} The reaction of indium trichloride with lithium aluminium hydride in ether solution at -70° yields the unstable compound $\text{In}(\text{AlH}_4)_3$, or, with a deficit of the lithium salt, $\text{InCl}_2(\text{AlH}_4)$. When this reaction is carried out at room

^{29a} Wiberg and Bauer, *Z. Naturforsch.*, 1951, 6b, 392.

^{29b} Wiberg and Usón, *ibid.*, 1951, 6b, 392.

^{29c} Wiberg and Schmidt, *ibid.*, 1951, 6b, 333.

³⁰ Wiberg and Johannsen, *Angew. Chem.*, 1942, 55, 38.

^{30a} Wiberg and Schmidt, *ibid.*, 1951, 6b, 171, 335; see also ref. 28.

temperature a white solid is precipitated which is probably polymerized InH_3 .^{30b}

Hydrides of Silicon, Germanium, Tin and Lead.

Silicon resembles carbon in forming a series of volatile hydrides, known as the silanes, corresponding to the saturated hydrocarbons, though it does not give volatile unsaturated hydrides. The formulæ and boiling-points are tabulated below (Table 9), together with data for the hydrocarbons.

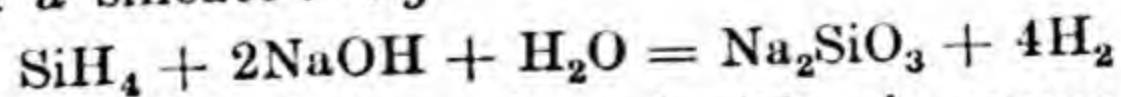
Table 9

Hydride	b.p.	Hydrocarbon	b.p.
SiH_4	- 111.9°	CH_4	- 161.3°
Si_2H_6	- 14.5°	C_2H_6	- 88.7°
Si_3H_8	52.9°	C_3H_8	- 44.5°
Si_4H_{10}	109°	$n\text{C}_4\text{H}_{10}$	0.5°
$\text{Si}_5\text{H}_{12}, \text{Si}_6\text{H}_{14}$	> 100°		

No evidence has been obtained that Si_4H_{10} consists of a mixture of isomers, but for Si_5H_{12} and Si_6H_{14} this is undoubtedly the case and a complete separation has not yet been effected with the small amounts of material available.

A mixture of these silicon hydrides is formed by the addition of 20 per cent hydrochloric acid to magnesium silicide (Mg_2Si), the rough proportions being: SiH_4 , 40; Si_2H_6 , 30; Si_3H_8 , 15; Si_4H_{10} , 10; higher hydrides, 5 per cent. They are separated and characterized in the same type of apparatus as is used in work with the boron hydrides. An alternative method is to add powdered magnesium silicide to a solution of ammonium bromide in liquid ammonia, which functions as an acid (*cf.* p. 506). By far the best method for preparing SiH_4 and Si_2H_6 , however, is the reduction of the corresponding chlorides with lithium aluminium hydride.

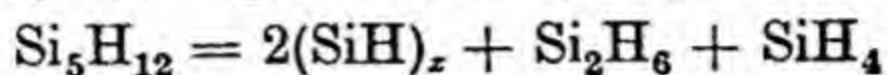
There is no reason to doubt that the structures of the silicon hydrides parallel those of the corresponding saturated hydrocarbons, though they are more reactive. Thus, although stable to water, all are decomposed by dilute alkali with evolution of hydrogen and formation of a silicate: *e.g.*



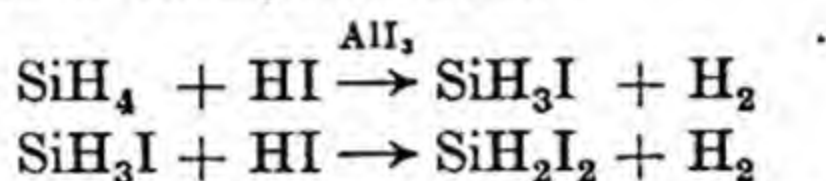
All are readily oxidized, monosilane igniting in oxygen at 100° and the higher members of the series becoming progressively more

^{30b} Wiberg and Schmidt, *ibid.*, 1951, 6b, 172.

inflammable. These ignition temperatures are much lower than those of the hydrocarbons. The thermal stability is also less and decreases with increasing molecular weight. All the hydrides are decomposed to silicon and hydrogen at *ca.* 500°, but at intermediate temperatures a process analogous to the cracking of hydrocarbons occurs, which may be represented by equations such as

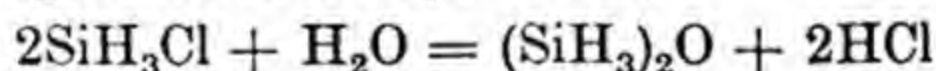


The hydrides are all strong reducing agents. They react explosively with chlorine or bromine at room temperature; the mono- and di-halogenated silanes are best prepared by the reaction of the hydrogen halide with the hydride at 100°, using the corresponding aluminium halide as a catalyst. Thus:



Very little of the trihalogenated product is formed in this reaction. Silicochloroform, SiHCl_3 , is, however, readily obtained by the action of hydrogen chloride on powdered silicon at 350°. The mixture of silicon tetrachloride and silicochloroform produced can be separated by distillation through an efficient fractionating column.

Zinc methyl reacts at low pressures with SiH_3Cl and SiH_2Cl_2 , forming the mixed hydrides $\text{SiH}_3(\text{CH}_3)$ and $\text{SiH}_2(\text{CH}_3)_2$. On hydrolysis of these with alkali only the radical containing silicon is attacked. The compound SiH_3Cl also reacts with water, forming the silicon analogue of dimethyl ether,



The reaction product from ammonia and excess of SiH_3Cl is $\text{N}(\text{SiH}_3)_3$, the silicon analogue of trimethylamine, which reacts with HCl , forming SiH_3Cl . It has no basic properties.



The corresponding reaction with methylamine gives $\text{NCH}_3(\text{SiH}_3)_2$, which is similarly decomposed by hydrogen chloride. Dimethylamine gives $\text{N}(\text{CH}_3)_2\text{SiH}_3$, which forms an unstable quaternary salt, while trimethylamine forms the stable solid quaternary compound $\text{N}(\text{CH}_3)_3\text{SiH}_3\text{Cl}$, which is a useful silylating reagent,³¹ reacting with alcohols to form silyl alkyl ethers, *e.g.*



Recently Burg and his co-workers³² have shown that trisilylamine has some of the co-ordinating properties of trimethylamine. Thus, for example, with boron trichloride the compound $(\text{SiH}_3)_3\text{NBCl}_3$ is

³¹ Emeléus and Miller, *J.C.S.*, 1939, 819.

³² Burg and Kuljian, *J. Amer. Chem. Soc.*, 1950, 72, 3103.

formed initially, but loses SiH_3Cl at -80° to give $(\text{SiH}_3)_2\text{NBCl}_2$. Trisilylamine and monobromo diborane gave $(\text{SiH}_3)_2\text{NBH}_2$, which reacted further to form $(\text{SiH}_3)_2\text{NB}_2\text{H}_5$. These and other similar preparations indicate that this field may be capable of considerable further development. Another related compound which merits further study is $((\text{C}_2\text{H}_5)_3\text{Si})_2\text{NK}$, formed by the reaction between $(\text{C}_2\text{H}_5)_3\text{SiH}$ and potassamide in liquid ammonia.³³ There is also some indication that the silyl radical may form the analogues of organometallic compounds (e.g. SiH_3ZnI), though this possibility has not yet been fully explored.³⁴

Decomposition of monosilane in an electric discharge yields a solid residue varying in composition between $\text{SiH}_{1.2}$ and $\text{SiH}_{1.4}$. A similar compound is formed when monosilane is decomposed in presence of mercury by irradiation with mercury resonance radiation. These compounds are not volatile or soluble in non-reactive solvents, and their molecular weights cannot therefore be determined. They dissolve in alkali with evolution of hydrogen. When calcium monosilicide (CaSi) is treated with absolute alcohol saturated with hydrogen chloride, or with glacial acetic acid, a light brown amorphous solid with the empirical formula $(\text{SiH}_2)_x$ is formed. This is spontaneously inflammable. It is hydrolysed by mineral acids with evolution of hydrogen ($\text{SiH}_2 + 2\text{H}_2\text{O} = \text{SiO}_2 + 3\text{H}_2$). A noteworthy feature of this hydrolysis is that no silicon hydrides are formed, whereas decomposition of the corresponding germanium compounds, GeH_2 (*vide infra*), yields germanous chloride, hydrogen and a mixture of hydrides. On heating $(\text{SiH}_2)_x$ at 380° it undergoes cracking with production of a range of saturated silicon hydrides.

Germanium Hydrides. Germanium resembles silicon closely in its capacity for hydride formation and in the methods of preparation. The known volatile compounds are:

<i>Hydride</i>	<i>m.p.</i>	<i>b.p.</i>
GeH_4	-165°	-90°
Ge_2H_6	-109°	29°
Ge_3H_8	-105.6°	110.5°

Dennis, Corey and Moore³⁵ first prepared a mixture of these hydrides by the action of dilute hydrochloric acid on magnesium germanide, Mg_2Ge . The separation is carried out by the technique used for the hydrides of boron and silicon. Monogermane has also been prepared by decomposing magnesium germanide with a solution of ammonium bromide in liquid ammonia, but the simplest method is to reduce an ethereal solution of germanium tetrachloride with

³³ Kraus and Nelson, *J. Amer. Chem. Soc.*, 1934, **56**, 195.

³⁴ Emeléus, Maddock and Reid, *J.C.S.*, 1941, 353.

³⁵ *J. Amer. Chem. Soc.*, 1924, **46**, 657.

lithium aluminium hydride. The polymerized hydride $(\text{GeH}_2)_x$, an amorphous yellow solid, is formed by decomposing calcium monogermanide with acids,



The three germanium hydrides decompose thermally at lower temperatures than do the silicon hydrides. They are less inflammable, though the ease of oxidation increases from monogermane to trigermane. They are unattacked by water and monogermane is not decomposed by 33 per cent alkali. This is a striking point of difference between monosilane and its germanium analogue. Digermane, however, does evolve hydrogen when treated with alkali.

Numerous halogenated derivatives of monogermane have been prepared. One of the most interesting of these, germanochloroform, GeHCl_3 , is a colourless liquid formed by the action of hydrogen chloride on germanous chloride at 40° ,³⁶ the latter being prepared by circulating germanium tetrachloride over germanium at 350° .³⁷

Structurally the germanium hydrides do not present any point of special interest: they are almost certainly analogous to the silicon hydrides. The compound $(\text{GeH}_2)_x$ is, however, interesting because of the well-defined divalent state of germanium. There is no evidence for its existence in a monomeric form and it has been suggested that the solid hydride is a chain-like polymer. It decomposes thermally at $120\text{--}220^\circ$ into a mixture of H_2 , GeH_4 , Ge_2H_6 and Ge_3H_8 .³⁸ With bromine, germanium tetrabromide and hydrogen bromide are produced, while with aqueous sodium hydroxide monogermane and hydrogen are evolved and the solution is found to contain sodium germanite, Na_2GeO_2 . In the dry state $(\text{GeH}_2)_x$ reacts explosively with oxygen.

Tin Hydride. This interesting compound is a gas boiling at -52° . Analysis and molecular weight determinations show it to have the formula SnH_4 . It was first prepared by Paneth and his co-workers³⁹ by decomposing a tin-magnesium alloy with dilute acids, by reducing tin dissolved in dilute sulphuric acid by the addition of magnesium powder or by the cathodic reduction of tin solutions with pure lead electrodes. All of these methods give poor yields, and the reduction of stannic chloride by lithium aluminium hydride is probably the best method of preparing the hydride in quantity.⁴⁰

³⁶ Dennis, Orndorff and Tabern, *J. Physical Chem.*, 1926, 30, 1049.

³⁷ Dennis and Hunter, *J. Amer. Chem. Soc.*, 1929, 51, 1151.

³⁸ Royen and Schwarz, *Z. anorg. Chem.*, 1933, 215, 295.

³⁹ *Ber.*, 1919, 52, 2020; 1922, 55, 769.

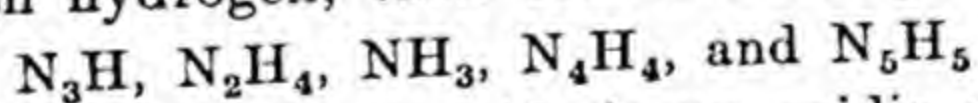
⁴⁰ Finholt, Bond, Wilzbach and Schlesinger, *J. Amer. Chem. Soc.*, 1947, 69, 2692.

Tin hydride, or monostannane as it is sometimes called, decomposes slowly at room temperature into tin and hydrogen. Decomposition is rapid at 150° . There is no evidence that higher hydrides are formed. It is unattacked by 15 per cent caustic soda and is also without action on solutions of copper sulphate or ferric chloride. It is, however, completely absorbed by solutions of silver nitrate or mercuric chloride.

Lead Hydride.—The formation of a volatile hydride of lead was first reported by Paneth and Norring.⁴¹ It was shown that the hydrogen formed when a magnesium lead alloy containing radioactive lead (ThB) was dissolved in hydrochloric acid carried with it a very small quantity of a volatile lead compound, which was detected by the radioactivity of the lead isotope mixed with the inactive lead in the alloy. Later, an electrolytic method was developed which gave improved, though very small yields. The hydride could be condensed out in liquid air and re-evaporated and also gave visible deposits of lead when passed through a hot tube. The compound decomposed at room temperature and was not analysed or characterized by physicochemical measurements. It is very probable, however, that it is the compound PbH_4 , the stability of which would be expected to be less than that of monostannane. No experiments have yet been described on the reduction of lead tetrachloride with lithium aluminium hydride.

Hydrides of Group V.

The volatile hydrides formed by the elements of Group V are for the most part well known, and an extensive review of their preparation and properties is not necessary. Nitrogen actually forms five compounds with hydrogen, their formulæ being



The first of these, hydrazoic acid, is an acidic substance, while N_4H_4 and N_5H_5 are ammonium azide and hydrazinium azide, respectively, and not true hydrides. The chemical reactions of ammonia are well known, and interesting properties of liquid ammonia solutions are reviewed in Chapter XVII, where it is shown that liquid ammonia behaves chemically as if it ionized into H^+ and NH_2^- . The H^+ is in equilibrium with neutral ammonia and the ammonium ion ($NH_3 + H^+ \rightleftharpoons (NH_4)^+$), while the NH_2^- ion is the counterpart of the hydroxyl ion in aqueous solutions, and gives amides of the type M^1NH_2 , corresponding to the hydroxides M^1OH .

The volatile phosphorus hydrides have the formulæ PH_3 and P_2H_4 . The first of these is very well known, although it may be

⁴¹ *Ber.*, 1920, 53, 1693; *Z. Elektrochem.*, 1920, 26, 452.

noted in passing that certain derivatives such as the partially halogenated phosphines have not yet been prepared. It is only recently, however, that the physical properties of P_2H_4 have been investigated with carefully purified material.⁴²

The existence of solid hydrides of phosphorus appears to be very uncertain in view of recent investigations. It was formerly believed that an insoluble yellow hydride of the formula $(P_2H)_x$ was formed in the decomposition of metal phosphides by water and in other reactions which yield phosphine, as well as in the decomposition of P_2H_4 . The molecular weight of this hydride was deduced from the lowering of the freezing-point of yellow phosphorus, and corresponded to the formula $P_{12}H_6$. The hydride was dissociated by heat into yellow phosphorus and phosphine, it ignited in air at about 120° , and was soluble in alcoholic alkalis, forming a red solution. From the latter fact it was supposed that at least one hydrogen atom in the molecule was acidic.

The formation of solid hydrides was questioned by Royen and Hill,⁴³ who find that the yellow solid formed in the decomposition of P_2H_4 is variable in composition, and amorphous when examined by means of X-rays. It evolves phosphine on heating, but no hydrogen is formed until the decomposition temperature of phosphine itself is reached. The solid hydride is regarded by these authors as an adsorption complex of phosphine on a yellow amorphous form of phosphorus, the dissolution of the solid in alcoholic alkali being attributed to peptization. It was considered, moreover, that the methyl and phenyl derivatives of $P_{12}H_6$ which had been described were not compounds, but adsorbates of methyl and phenyl phosphine on yellow amorphous phosphorus. It may be added in this connexion, that although Royen and Hill's conclusions are fairly convincing they may not apply to all the possible methods of preparing the solid 'hydride'.

Arsenic, Antimony and Bismuth Hydrides.—The volatile hydrides of arsenic and antimony need no description here as both are very well known. The hydride of bismuth would be expected from the position of the element in the Periodic Table to be very unstable and to be detectable only with difficulty. Its formation was first proved by Paneth by making use of the radioactive indicator method.⁴⁴ An alloy of magnesium and thorium-C, which is a radioactive isotope of bismuth, was dissolved in dilute hydrochloric acid, and it was found that the hydrogen given off was mixed with a condensable gas which had the radioactive characteristics of

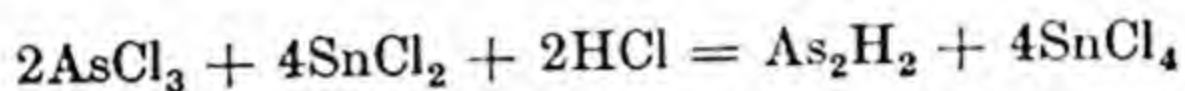
⁴² Royen and Hill, *Z. anorg. Chem.*, 1936, 229, 97.

⁴³ *Ibid.*, 1936, 229, 369; 1938, 235, 324.

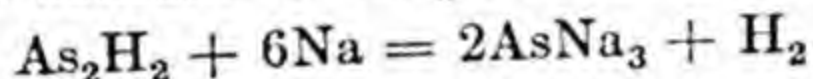
⁴⁴ *Ber.*, 1918, 51, 1704; *Z. Elektrochem.*, 1918, 24, 298.

thorium-C. Later the hydride was formed by dissolving a magnesium-bismuth alloy in acid, and was shown to be a volatile substance which was decomposed rapidly at temperatures above 150° , giving a deposit of bismuth. This compound has not been prepared in sufficient quantities for an investigation of its physical properties to be carried out, but the boiling-point has been estimated by extrapolation from values for the other hydrides of the series as $+22^{\circ}$.⁴⁵

The formation of a solid arsenic hydride of the formula $(\text{As}_2\text{H}_2)_x$ has been known since the time of Davy. Weeks and Druce⁴⁶ prepared this substance in good yield by adding a solution of arsenic trichloride in hydrochloric acid to an ethereal solution of stannous chloride,



The hydride is precipitated as a brown amorphous powder. Montignie⁴⁷ has studied some of the reactions of As_2H_2 , finding it to be insoluble in cold water but decomposed by boiling water with liberation of hydrogen ($\text{As}_2\text{H}_2 + 3\text{H}_2\text{O} = \text{As}_2\text{O}_3 + 4\text{H}_2$). It undergoes slow spontaneous decomposition at room temperature into arsenic and hydrogen and has strong reducing properties. The reaction with hot sodium takes place according to the equation



In spite of this seemingly definite chemical evidence, there is still some doubt as to the nature of the compound. Its structure and molecular weight are completely unknown. The same is true of a second solid hydride which is said to be formed in the oxidation of arsine with a solution of stannic chloride in hydrochloric acid ($4\text{AsH}_3 + 5\text{SnCl}_4 = \text{As}_4\text{H}_2 + 10\text{HCl} + 5\text{SnCl}_2$).⁴⁸

Hydrides of Group VI.

Sulphur Hydrides.—In addition to the familiar compound H_2S , sulphur forms the compounds H_2S_2 , H_2S_3 , H_2S_4 , H_2S_5 and H_2S_6 . All are obtained by decomposing polysulphides with acids. If a solution of sodium polysulphide is prepared by the addition of sulphur to a solution of sodium sulphide, and then poured into hydrochloric acid cooled to -10° , a yellow oil separates. It can be separated, dried and distilled at low pressures, when two definite compounds, H_2S_2 and H_2S_3 , can be separated. Recently the three remaining compounds have been isolated in a pure state from this

⁴⁵ Paneth, *Radio Elements as Indicators*, Cornell University Press, 1928.

⁴⁶ *Chem. News*, 1924, 129, 31; *Rec. trav. Chim.*, 1925, 44, 970.

⁴⁷ *Bull. Soc. Chim.*, 1935, 2, 1020.

⁴⁸ Moser and Brukl, *Monatsh.*, 1924, 45, 25.

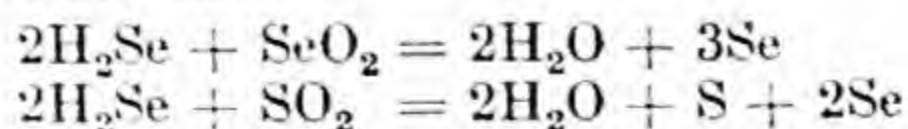
source by special distillation procedures.⁴⁹ The compound H_2S_5 has also been obtained by decomposing ammonium pentasulphide with anhydrous formic acid.

The polysulphides of hydrogen are all rather unstable yellow liquids which decompose readily into hydrogen sulphide and sulphur. The decomposition is catalysed by a trace of alkali. Stable solutions are formed in solvents such as benzene, chloroform, carbon disulphide and ether and the molecular weights may thus be verified by cryoscopic measurements. All of the hydrogen polysulphides are able to dissolve sulphur. Definite crystalline addition compounds are formed with certain organic substances. Among these are the compounds with brucine ($\text{C}_{21}\text{H}_{22}\text{N}_2\text{O}_2$, H_2S_6), strychnine ($\text{C}_{23}\text{H}_{26}\text{N}_2\text{O}_4$, H_2S_6), benzaldehyde ($\text{C}_6\text{H}_5\text{CHO}$, H_2S_3) and benzoquinone ($\text{C}_6\text{H}_4\text{O}_2$, H_2S_5).

The structure of the polysulphides has not yet been fully elucidated, but there is a good deal of evidence that they contain a chain of linked sulphur atoms with terminal hydrogen atoms which are acidic. The crystalline compound BaS_3 has been shown by X-ray analysis to contain the ion $(\text{S}-\text{S}-\text{S})^{2-}$, the valency angle of which is 103° . Electron diffraction and Raman spectrum measurements have established the structural resemblance between H_2S_2 and H_2O_2 . Evidence obtained with organic polysulphides also shows that for the types R_2S_2 and R_2S_3 (where R is an organic radical) there is a chain of sulphur atoms. It is not yet clear, however, if the S_4 , S_5 and S_6 groups form branched or unbranched chains.

Selenium and Tellurium Hydrides.

Selenium and tellurium both differ from sulphur in that up to the present only one hydride has been prepared from each element. The hydride H_2Se was discovered in 1817, and is a gas which boils at -41.2° , and which may conveniently be prepared by decomposing aluminium selenide with water. Hydrogen and selenium react at temperatures above 250° , with formation of a certain amount of hydrogen selenide. It differs from hydrogen sulphide in being decomposed readily by moist oxygen with precipitation of selenium and formation of water. It reacts either with selenium dioxide or with sulphur dioxide thus:



Hydrogen selenide in aqueous solution is more strongly acidic than is hydrogen sulphide. It reacts with metal salts in solution and

⁴⁹ Feher and Bandler, *Z. Elektrochem.*, 1941, **47**, 844; *Z. anorg. Chem.*, 1947, **253**, 170; **254**, 170, 289.

precipitates selenides, but these are generally contaminated with free selenium. Although hydrogen polyselenides are unknown, metallic polyselenides of the type $M_2^xSe_x$ are known, in which x can have values up to 5, and stable organic derivatives such as benzyl diselenide have also been prepared.

Hydrogen telluride, H_2Te , is a gas boiling at -0.6° , and is less stable than the selenide, being endothermic to the extent of $-35,000$ g. cal., whereas hydrogen selenide is considerably less so (*circa* $-18,000$ g. cal.). The hydride is decomposed immediately by moist air, with deposition of tellurium. It is also very sensitive towards the halogens, the corresponding hydrogen halide being formed on mixing it with chlorine, bromine, or iodine. The instability of the substance is also apparent from the fact that it will reduce ferric salts to the ferrous state or mercuric salts to mercurous salts, with precipitation of elementary tellurium.

Polonium Hydride.

The formation of a hydride of polonium would be expected from its position in the Periodic Table, and has actually been observed by using the radioactivity of polonium itself as an indicator for detecting the formation of a volatile compound. It is formed together with hydrogen by deposition of polonium on a magnesium foil, followed by dissolution of the foil in acid. It was found in this experiment that the gas evolved when the metal was dissolving was radioactive. The radioactive component could, however, be frozen out by cooling the gas stream to -80° , and was re-evaporated on raising the temperature once more. The quantities of this hydride were extremely small, being of the order of 10^{-13} to 10^{-16} gram, and the formula has not been determined. It would be expected, however, from the position of polonium in the Periodic Table, to be PoH_2 .

Interstitial Hydrides.

A number of transition metals possess the remarkable property of absorbing relatively large amounts of hydrogen when heated to moderate temperatures. Interstitial hydrides are formed which are related to other interstitial compounds such as borides, carbides and nitrides in the sense that the lattice of the parent metal may undergo no change. It is, however, expanded in order to accommodate the hydrogen. This can be established both by X-ray and density measurements. The absorption of hydrogen is reversible and it can in every case be removed by pumping at a sufficiently high temperature. Hydrogen, like the other elements which form interstitial compounds, has a relatively small atom ($r = 0.37 \text{ \AA}$).

The adsorption of hydrogen by palladium is the most familiar example of this phenomenon. One volume of the metal will absorb up to 900 volumes of hydrogen. More is taken up by finely divided than by massive metal, and the amount at saturation decreases with increasing temperature. The lattice of the metal is expanded and the conductivity falls, though the characteristics of metallic conduction are retained. Hydrogen discharged electrolytically at a palladium cathode is also absorbed and the metal charged with hydrogen in this way has strong reducing properties. It will, for example, precipitate metallic mercury from a solution of mercuric chloride and will reduce ferric salts to the ferrous state.

Considering other cases, thorium begins to absorb hydrogen at 400° , giving a product approximating to the composition ThH_2 when cooled from a high temperature in an atmosphere of the gas.⁵⁰

The behaviour of zirconium is very similar, while titanium and tantalum have given products with the formulæ $\text{TiH}_{1.73}$ and $\text{TaH}_{0.76}$, respectively.⁵¹ These are black powders which are stable in air. Metallic vanadium absorbs hydrogen at room temperature, the formula of the product, which is readily oxidized in air, approximating to $\text{VH}_{0.6}$.⁵² Cerium, lanthanum and praseodymium also absorb hydrogen when heated. The formulæ of the products approximate to $\text{CeH}_{2.8}$, $\text{PrH}_{2.7}$ and $\text{LaH}_{2.8}$, although here again it must be pointed out that the amount of hydrogen taken up is a function of the experimental conditions, and that these formulæ do not necessarily represent saturation values.

Sieverts and his co-workers have investigated the heats of formation of a number of these hydrides, and have shown that they are positive and in some cases comparable in magnitude with values for salt-like hydrides. This is illustrated by the data tabulated below, which refer to the heat evolved in the combination of one gram molecule of hydrogen with the metal. The heats of formation were measured in some instances by direct determinations of the heats of combustion and in others by calorimetric determinations of the heat of solution of the metal and of its hydride in a suitable acid.

The high values for certain of the hydrides suggest that there can be little difference in the type of chemical binding in a substance such as lanthanum hydride and in, say, calcium hydride. Typical data for salt-like hydrides are included in the table.

⁵⁰ Sieverts, Gotta and Halberstadt, *Z. anorg. Chem.*, 1930, 187, 155.

⁵¹ Sieverts and Roell, *Z. anorg. Chem.*, 1926, 153, 289; Sieverts and Gotta, *ibid.*, 1930, 187, 155; 1931, 199, 384.

⁵² Huber, Kirschfeld and Sieverts, *Ber.*, 1926, 59, 2891.

Table 10

Hydride	Heat of formation (g. cal./g. mol. of H_2)	Hydride	Heat of formation (g. cal./g. mol. of H_2)
$LaH_{2.76}$. .	40,090	LiH . . .	43,200
$CeH_{2.69}$. .	42,260	NaH . . .	33,200
$PrH_{2.85}$. .	39,520	CaH_2 . . .	46,600
$TiH_{1.73}$. .	31,100	SrH_2 . . .	42,200
$ZrH_{1.98}$. .	39,900	BaH_2 . . .	40,960
$TaH_{0.78}$. .	Slightly +		
$PdH_{0.6}$. .	9,280		

Density determinations have also been carried out.⁵³ They show that the salt-like hydrides are always denser than the parent metal, whereas the interstitial hydrides are less dense. Data illustrative of this point are given below. In each case the percentage change in density in forming the hydride from the metal is quoted.

Table 11

Hydride	Δd in forming hydride (%)	Hydride	Δd in forming hydride (%)
$TiH_{1.73}$. .	- 15.5	LiH . . .	+ 52.8
$ZrH_{1.92}$. .	- 13.2	NaH . . .	+ 44
$TaH_{0.76}$. .	- 9.1	CaH_2 . . .	+ 10
$CeH_{2.69}$. .	- 17.5	BaH_2 . . .	+ 20
$VH_{0.56}$. .	- 6.7		

The re-examination of certain of the interstitial hydrides in recent years has shown that both the rate at which hydrogen is taken up by a metal and its amount are increased by the use of pure metals and pure hydrogen. In the case of titanium, for example, a stoichiometric compound TiH_2 has been prepared.^{53a} This does not entirely vitiate the general conclusions to be drawn from earlier work. It does, however, bring sharply into focus the problem of determining the nature of the valency forces in these hydrides. The case of uranium hydride, which is considered below, is typical of the trend of current investigations.

Uranium Hydride.—When uranium metal is heated to 250–350° in hydrogen the gas is rapidly absorbed and a black powder of the

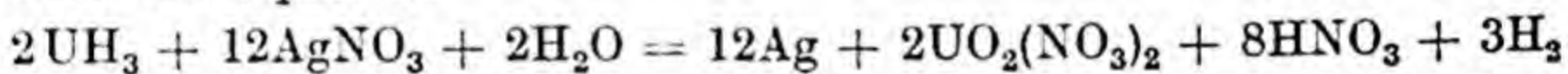
⁵³ Sieverts and Gotta, *Z. Elektrochem.*, 1926, 32, 102; *Z. anorg. Chem.*, 1930, 187, 155.

^{53a} Gibb and Kruschwitz, *J. Amer. Chem. Soc.*, 1950, 72, 5365; Gibb, McSharry and Braydon, *ibid.*, 1951, 73, 1751.

composition UH_3 is formed. The reaction with deuterium is similar. Absorption of hydrogen occurs at lower temperatures if the hydrogen pressure is increased. At 450° the compound loses hydrogen forming uranium metal, which is finely divided and highly reactive.⁵⁴

At first sight uranium hydride might be thought to be an interstitial compound, but X-ray examination of the solid shows it to have a structure which is quite distinct from that of the three forms of uranium metal.⁵⁵ The hydride has a cubic lattice ($a = 6.631 \text{ \AA}$ for UH_3 ; 6.620 \AA for UD_3) in which the bonding between metal atoms is of little importance. The hydride has, however, the conducting properties of a metal and it has been suggested by Rundle that metal-hydrogen bonds play an important role in determining the structure, the hydrogen bridging metal atom to metal atom. Rundle has described the structure in terms of electron-deficient 'half bonds' of a type used in interpreting the structures of certain interstitial carbides, nitrides and metallic oxides.⁵⁶ This approach explains both the uranium-uranium distances in the compound and gives satisfactory positions for the correct number of hydrogen atoms.⁵⁷

Uranium hydride is pyrophoric and is also reactive towards a number of common reagents. It behaves as a strong reducing agent, silver being precipitated from silver nitrate in accordance with the equation



Cupric sulphate and mercuric chloride were also reduced to metal. The hydride was also found to be a convenient intermediate for the preparation of tri- and tetravalent uranium compounds. Thus when HCl was passed over UH_3 at $250\text{--}300^\circ$, UCl_3 was formed, while with HF the tetrafluoride UF_4 resulted.

Other Metallic Hydrides.

Copper Hydride.—The formation of a hydride of copper of the formula CuH has been known for some time. It is prepared by the action of sodium hypophosphite on a moderately dilute solution of cupric sulphate at 70° . The product obtained if this reaction is carried out at ordinary temperatures is contaminated with cuprous oxide and cupric phosphate, but at the higher temperature only copper hydride is formed. It is an unstable reddish-brown solid, the hydrogen content of the dry material being always

⁵⁴ Spedding *et al.*, *Nucleonics*, 1949, 4, 17, 43.

⁵⁵ *J. Amer. Chem. Soc.*, 1947, 69, 1719.

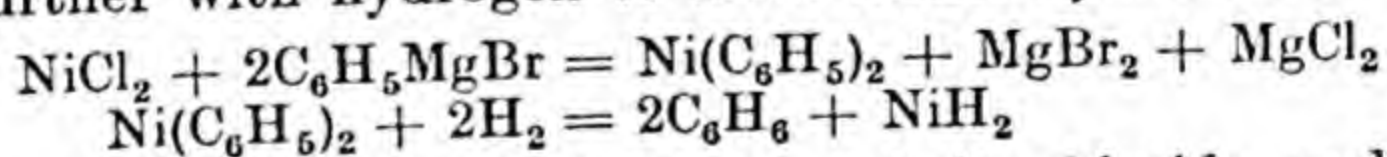
⁵⁶ Rundle, *Acta Crystallographica*, 1948, 1, 180.

⁵⁷ See also Pauling and Ewing, *J. Amer. Chem. Soc.*, 1948, 70, 1660.

short of the value corresponding to the formula CuH .⁵⁸ It decomposes into copper and hydrogen when heated in the dry state above 60° , takes fire in chlorine, and yields hydrogen when treated with dilute hydrochloric acid, although not with water. The heat of formation was measured by Sieverts and Gotta⁵⁹ by dissolving CuH in a solution of cupric chloride in hydrochloric acid, and then dissolving copper in the same solvent. The value obtained was -5120 g. cal. per g. mol.

The nature of copper hydride is not yet fully established. Metallic copper has a low adsorptive capacity for hydrogen, and it is very doubtful if the product prepared as described bears any relation to adsorption products obtained from the metal. Classification as a salt-like hydride is scarcely justified in view of the negative heat of formation, while X-ray data⁶⁰ show a face-centred cubic lattice, similar to that of copper but with the copper atoms farther from one another, presumably on account of the introduction of hydrogen into the lattice. Copper hydride may perhaps be grouped with the hydrides of nickel, cobalt, iron and chromium which were prepared by Weichselfelder, and which are described below, but the evidence for a final decision of this point is still lacking.

Hydrides of Nickel, Cobalt, Iron and Chromium.—Weichselfelder⁶¹ found that on passing hydrogen through a suspension of powdered anhydrous nickel chloride in an ether solution of phenyl magnesium bromide, four atoms of hydrogen were absorbed per atom of nickel and a black precipitate was formed which evolved hydrogen on treatment with water, alcohol or dilute acids. In the dry state this black substance was found to have a composition represented by the formula NiH_2 . It is believed that the initial product of this reaction may be nickel diphenyl $\text{Ni}(\text{C}_6\text{H}_5)_2$, and that this reacts further with hydrogen to form nickel hydride and benzene



The reaction between anhydrous cobalt chloride and phenyl magnesium bromide is similar to the above, although the absorption of hydrogen takes place more slowly. Analysis of the product corresponds to the formula CoH_2 . With anhydrous ferrous chloride the hydride FeH_2 was prepared in the same way, but with ferric chloride the absorption of hydrogen was more vigorous. A black precipitate was formed, which lost hydrogen in the process of

⁵⁸ Hüttig and Brodkorb, *Z. anorg. Chem.*, 1926, 153, 235.

⁵⁹ *Annalen*, 1927, 453, 289.

⁶⁰ Hüttig and Brodkorb, *Z. anorg. Chem.*, 1926, 153, 242.

⁶¹ *Annalen*, 1926, 447, 64.

drying. The analytical data pointed in this case to the formation of the hydride FeH_6 . Anhydrous chromic chloride, dissolved in an ether solution of phenyl magnesium bromide, likewise absorbed hydrogen slowly. The product had the composition CrH_3 . It is probable that yet other solid metallic hydrides will be produced by the reduction of metallic derivatives with lithium aluminium hydride and similar powerful reducing agents.

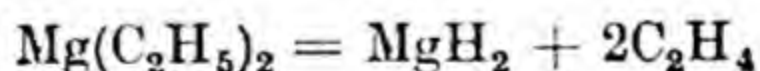
There is no indication at present of the true nature of these hydrides. The method of their preparation does not suggest any analogy with substances such as the rare earth hydrides, nor is there any reason to suppose that, say, chromium hydride prepared by Weichselfelder's reaction bears any relation to the product obtained when metallic chromium adsorbs hydrogen. Until essential data such as heats of formation and lattice dimensions are available for the above compounds there appears to be little prospect of definite progress towards their classification.

Hydrides of Zinc, Cadmium, Beryllium and Magnesium.—A hydride of zinc of the formula ZnH_2 has been prepared by the interaction of dimethyl zinc with a diethyl ether solution of lithium aluminium hydride.⁶²



The compound has also been prepared by an analogous reaction from zinc iodide.⁶³ It decomposes above 80° to zinc and hydrogen. Cadmium hydride, which was obtained similarly from dimethyl cadmium, underwent rapid decomposition above 0° . Both compounds are white non-volatile solids, which do not dissolve in ether and are slowly decomposed by water. Their structures have not yet been determined.

The hydride BeH_2 has been prepared by the reaction of lithium aluminium hydride in ether solution with dimethyl beryllium⁶² or beryllium chloride.⁶⁴ Its stability is similar to that of ZnH_2 . Both compounds react with diborane and form the metal borohydride. A similar procedure has been applied to prepare magnesium hydride, MgH_2 .⁶² This is also formed in the pyrolysis of magnesium diethyl in vacuum at 175° .⁶⁵



The compound MgC_2H_4 is formed simultaneously. The hydride decomposes at $280\text{--}300^\circ$ to magnesium and hydrogen and reacts

⁶² Barbaras, Dillard, Finholt, Wartik, Wilzbach and Schlesinger, *J. Amer. Chem. Soc.*, 1951, **73**, 4585.

⁶³ Wiberg, Henle and Bauer, *Z. Naturforschg.*, 1951, **6b**, 393.

⁶⁴ Wiberg and Bauer, *ibid.*, 1951, **6b**, 171.

⁶⁵ Wiberg and Bauer, *ibid.*, 1950, **5b**, 396.

with diborane to form $\text{Mg}(\text{BH}_4)_2$. A total synthesis of MgH_2 in 60 per cent yield is also possible by the interaction of magnesium and hydrogen in presence of magnesium iodide at $570^\circ/200$ atm.⁶⁶ Wiberg has suggested that the structure of magnesium hydride may involve hydrogen bridges between the metal atoms, which is believed to be the case in polymerized aluminium hydride, but in neither case is there any evidence.

⁶⁶ Wiberg, Goeltzer and Bauer, *ibid.*, 1951 6b, 394.

CHAPTER IX

FREE RADICALS OF SHORT LIFE¹

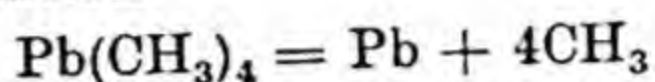
The chemical radical was recognized in 1832 by Liebig and Wöhler as a group of atoms capable of occurring intact in a number of compounds and of being replaced by other elements or radicals. This conception was supported by Kolbe's work (1849) on the electrolysis of sodium acetate, when 'free methyl' was considered to be formed, and also by Frankland's preparation of 'free ethyl' by the interaction of zinc and ethyl iodide. These substances we now know to be twin radicals, and the same is true of Bunsen's 'free cacodyl', as well as of 'free cyanide' which was discovered by Gay-Lussac. The natural reaction of chemists to these early experiments was that while the existence of radicals in chemical compounds was generally admitted, their isolation was regarded as impossible. Indeed, it was not until 1900, when Gomberg prepared triphenyl methyl, $C(C_6H_5)_3$, that the existence of free radicals received its first direct proof.

Triphenyl methyl was found to behave as a highly unsaturated compound. Thus it reacted readily with oxygen, yielding $(C_6H_5)_3C-O-O-C(C_6H_5)_3$, and was also capable of adding on halogens at 0° . It was shown from determinations of the molecular weights in various solvents that the substance was an equilibrium mixture of triphenyl methyl and hexaphenyl ethane. The isolation of triphenyl methyl was followed by a large amount of research during which many similar bodies were prepared, and as a result these 'free radicals of long life' became well established as chemical individuals.

Free radicals such as methyl, CH_3 , and ethyl, C_2H_5 , were postulated as intermediaries in chemical reactions, but the first direct demonstration of their transitory existence is due to Paneth and Hofeditz. These investigators pumped the vapour of lead tetramethyl mixed with pure hydrogen or nitrogen as a carrier gas at a total pressure of 1.5–2.0 mm. of mercury through a heated quartz tube. Very high streaming rates were obtained by using pumps

¹ For a discussion of the physicochemical aspects of this topic see 'Atomic and Free Radical Reactions', by E. W. R. Steacie (American Chemical Society Monograph No. 102, 1946). See also Bawn, *J.C.S.*, 1949, 1042.

of high capacity, and a short section of the quartz tube was heated with a Bunsen burner. This resulted in decomposition of the lead alkyl with deposition of lead immediately beyond the heated zone. The gas passing away from the heated zone was reactive; it was able to eat away cold mirrors of lead, zinc, bismuth, or antimony, even when the latter were situated at distances up to 30 cm. from the heated portion of the tube. It was shown that the attack of the mirrors led to formation of the corresponding metal methyl. The active material must therefore have been free methyl, formed according to the equation



This method of producing free methyl radicals is illustrated by the diagram below (Fig. 47).

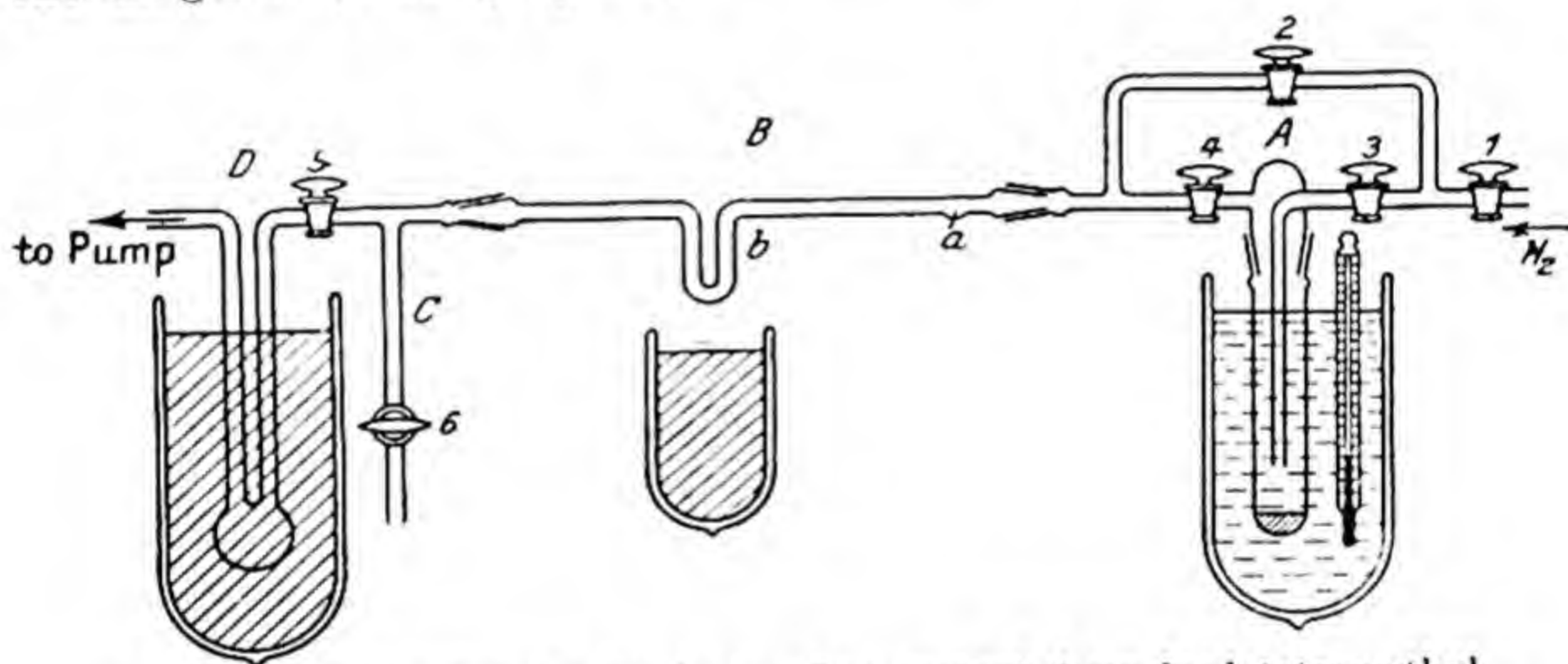


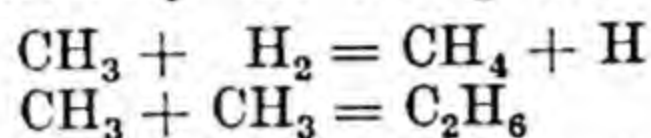
FIG. 47.—Apparatus for producing free methyl from lead tetramethyl.

Pure dry hydrogen was passed over the surface of lead tetramethyl cooled to -70° to -80° , and by suitable regulation of taps 2, 3 and 4, a mixture of hydrogen and lead tetramethyl vapour could be passed through the apparatus at a pressure of 1.5–2 mm. of mercury. By heating a small section of the quartz tube B with a Bunsen burner, or an electrical heating spiral, the lead alkyl was decomposed and a deposit of lead was formed. After this lead mirror had been allowed to cool a second spot on the quartz tube to the right of the first was heated. A new mirror formed at the heated spot, but while it was forming it was observed that the first mirror was eaten away. The experiment suggested, in fact, that some aggressive agent was being liberated in the decomposition of the metal alkyl.

This aggressive agent (which is actually free methyl) was formed by the decomposition of other metal methyls. Bismuth methyl, for example, when decomposed gave a substance which would eat

away lead mirrors, and the active material from lead methyl would eat away bismuth mirrors. Antimony and zinc mirrors could also be removed, and the compound from zinc was identified as zinc dimethyl. Numerous other methyl derivatives have since been identified as formed by this method, leaving no doubt as to the reality of the free methyl radical.

The concentration of free methyl in the gas stream may be judged from the time in which a mirror of standard opacity disappears. This time increases as the distance of the mirror from the heated zone is increased. Paneth found that when hydrogen was used as carrier gas for methyl radicals from lead tetramethyl the radicals disappeared by the two processes



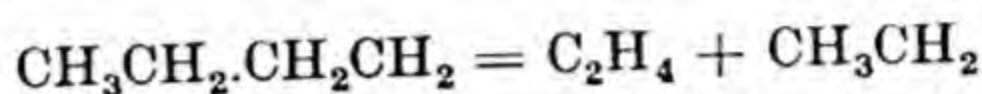
Low concentrations of radicals and increase in temperature resulted in the formation of less ethane and more methane. As would be expected, the use of helium in place of hydrogen as a carrier gas largely eliminated the formation of methane, and also increased the life of the radicals. By employing helium as carrier gas and heating the walls of the quartz tube, the half-value period of methyl could be raised to 0.1 second.

The life period of these free radicals is always expressed by the time needed for the concentration, as measured by the time of removal of a standard mirror, to fall to half its value. Experimentally such a determination is fairly readily carried out. The mirror is prepared by very careful volatilization of the substance to be examined until a film is formed which matches in opacity and extent some standard mirror. This matching process is not unlike the matching of mirrors against standards in the Marsh test for arsenic. Such a standard mirror is then prepared in consecutive experiments at a series of distances from the heated zone and the time of its disappearance is measured for each location. The reciprocal of this time is a measure of the concentration of radicals. The half-value period can then be deduced, knowing the streaming velocity and the distances of the mirrors from the heated zone.

The above experimental method was extended by Paneth and Lautsch² to the identification of free ethyl as a product of the thermal dissociation of lead tetraethyl, but attempts to prepare radicals such as propyl and butyl by this method, starting from the corresponding metal alkyl, were unsuccessful and yielded only methyl and ethyl radicals. This indicated that, if formed, these

² *Ber.*, 1931, 64, 2702.

higher radicals (*e.g.* butyl, C_4H_9) must decompose, either at the instant of their formation or very shortly afterwards, into simpler radicals. The experimental method would naturally fail to detect radicals which had almost completely combined or reacted before they could arrive at the metal mirror with the highest flow-rate obtainable. Frey and Hepp have, however, obtained evidence of the transitory formation of free butyl in the thermal decomposition of mercury dibutyl at $350-450^\circ$,³ although no derivative of the radical was isolated. Very careful analyses of the products of decomposition of the mercury alkyl were carried out, and it was shown that the radical probably decomposes according to the reaction



This agrees with Rice's general conclusions as to the mechanism of pyrolysis of organic compounds, which are discussed in the next section. The benzyl radical, $C_6H_5CH_2$, has also been identified as being formed by heating the vapour of tin tetrabenzyl. Benzyl was found to attack mirrors of selenium, tellurium, and mercury, the compound formed with mercury being identified as dibenzyl mercury, while with selenium a product was obtained from which dibenzyl selenide was isolated.⁴ The life period of benzyl in a cold tube was considerably shorter than that of methyl, but in a heated tube the radical had about the same half-value period, namely 6×10^{-3} second.

The methyl and ethyl radicals were used by Paneth and Loleit in synthesizing two new compounds of antimony, antimony cacodyl and its ethyl analogue, which had not been prepared before.⁵ The products formed by methyl radicals (Me) and ethyl radicals (Et) with mirrors of arsenic, antimony, and bismuth are shown in the table below.

		<i>Trialkyl</i>	<i>Dialkyl</i>	<i>Other products</i>
<i>Arsenic</i>	Me	$AsMe_3$	$(AsMe_2)_2$	$(AsMe)_3 ?$
	Et	$AsEt_3$	$(AsEt_2)_2$	$(AsEt)_3 ?$
<i>Antimony</i>	Me	$SbMe_3$	$(SbMe_2)_2$	
	Et	$SbEt_3$	$(SbEt_2)_2$	
<i>Bismuth</i>	Me	$BiMe_3$	$(BiMe_2)_2$	
	Et	$BiEt_3$		

All of these products except $(SbEt_2)_2$ and $(BiMe_2)_2$ were obtained by passing the radicals over the cold mirrors, but for the two substances specified, which are appreciably less volatile than the others, it was necessary to heat the mirror.

Production of Free Radicals by Pyrolysis of Organic Compounds.—The proof that free radicals are formed in the pyrolysis

³ *J. Amer. Chem. Soc.*, 1933, 55, 3357.

⁴ Paneth and Lautsch, *J.C.S.*, 1935, 380.

⁵ *Ibid.*, 1935, 366.

of organic compounds has been furnished very largely by the work of F. O. Rice.⁶ The vapours of the organic compounds, which included hydrocarbons, ketones, aldehydes, amines and ethers, were streamed through a quartz tube which was heated to 700–1000°, and the gas stream leaving the furnace was allowed to impinge on a cold mercury surface. The mercury alkyls formed distilled away and were condensed in a liquid air trap. After the run they were treated with an alcoholic solution of mercuric bromide, with which they reacted forming alkyl mercury bromides of the type RHgBr . These mercury bromide derivatives could be separated

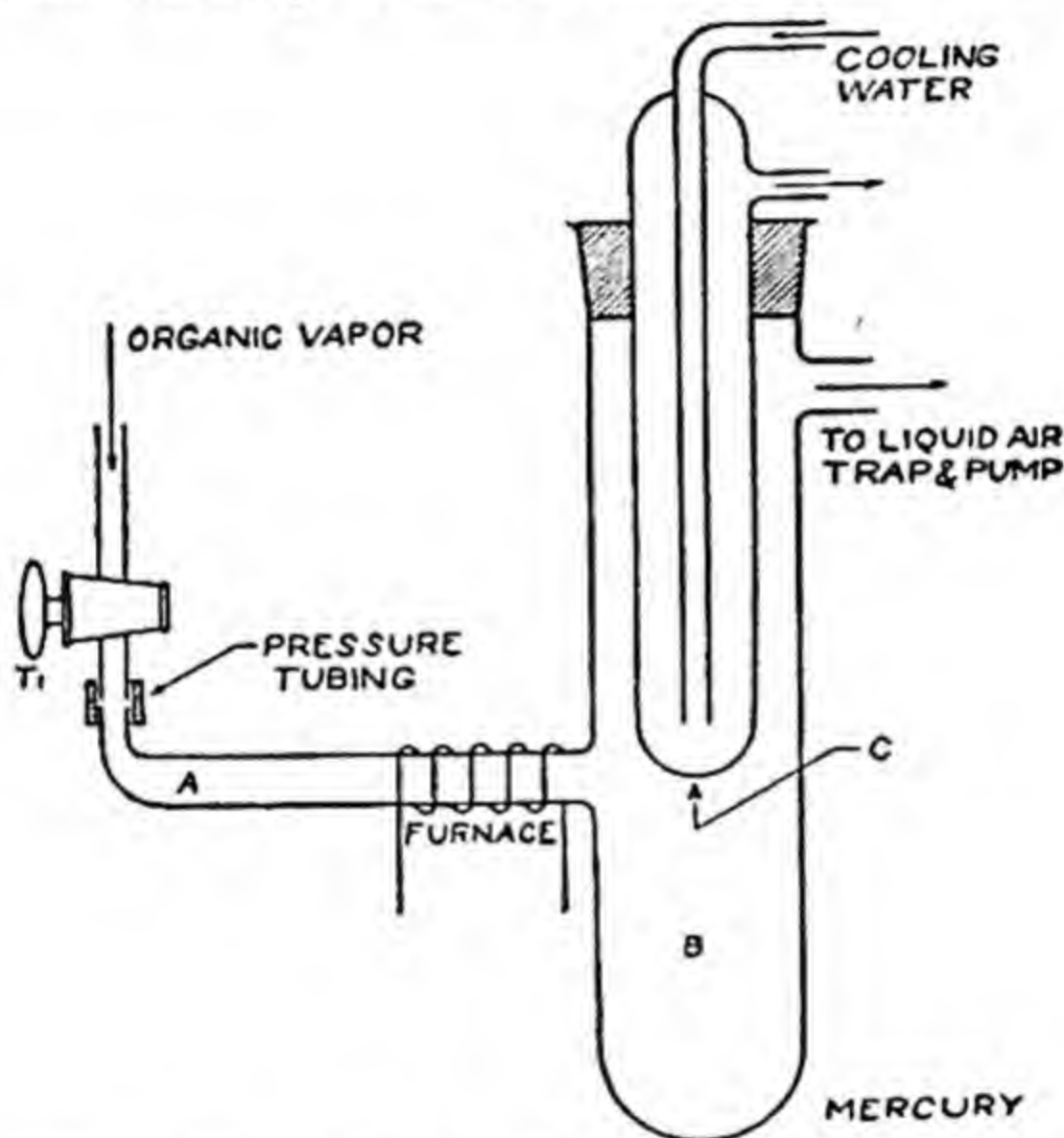


FIG. 48.—Apparatus for identification of free radicals produced by pyrolysis of organic compounds.

from one another, if necessary, by fractional sublimation and identified by means of their melting-points. The actual apparatus used in these experiments is illustrated by Fig. 48. The mercury was condensed on the water-cooled tube *C* by heating *B*. The main furnace tube and the tube holding the mercury were made of silica.

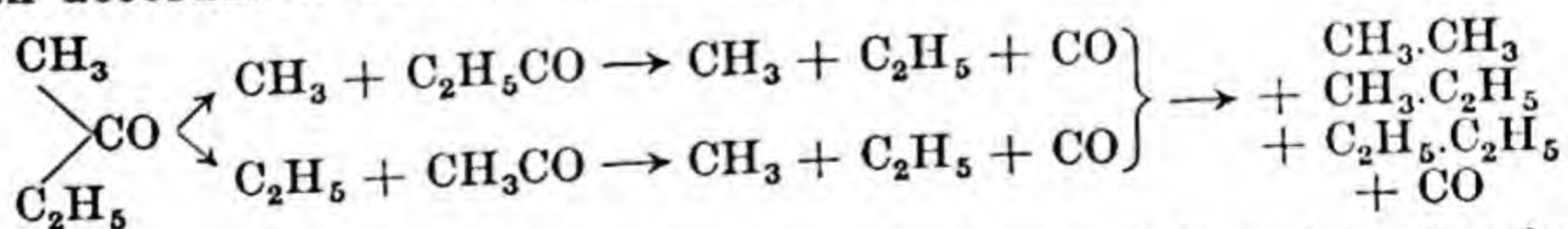
This method of carrying out the pyrolysis of organic compounds gave relatively large yields of radicals, but the only radicals identified by means of it were free methyl and ethyl. The situation may be summarized in Rice's own words: 'We looked very carefully for evidence of the formation of propyl and higher radicals, but could find no evidence whatsoever of their presence. The

⁶ Cf. *Trans. Faraday Soc.*, 1934, 30, 152.

higher alkyl mercuric bromides are appreciably more volatile than are the methyl and ethyl compounds and should therefore be readily detected even in small quantities.'

The very wide range of compounds studied by Rice and his co-workers and the relatively large amounts of material with which their experimental method permitted them to work would almost certainly have shown the presence of higher radicals had they been formed. It must be concluded, therefore, that if they are formed, radicals such as propyl or butyl must break down into methyl and ethyl at the high temperatures employed in the experiments of Paneth and of Rice. This leads one naturally to turn to methods which would produce these radicals of high molecular weight at lower temperature, so as to avoid decomposing them as soon as they are formed. One such method would be to decompose the organic vapour by streaming it through an electrical discharge. Some preliminary experiments of this nature have been made by Rice and Whaley,⁷ but, apart from showing that radicals are formed in a discharge, they have furnished us with little precise information. The second method of producing radicals at low temperature would be by decomposing organic compounds by means of light. As will be seen in the next section, this method has been applied with great success by Pearson, and has been the means of adding several new free radicals to the list of those known to the chemist.

Photochemical Production of Free Radicals.—The production of free radicals in photochemical processes was first deduced from the nature of the products of photolysis. If, for example, we consider the decomposition of methyl ethyl ketone by light of wave-lengths less than 3100 Å., it is found that the products consist largely of a mixture of ethane, propane, and butane in about equal proportions, together with carbon monoxide in equivalent amount.⁸ This is taken as evidence that the ketone is decomposed by light in accordance with the following scheme:



This reaction is typical of many which are believed to involve the production of free radicals. Among them the production of free methylene, CH_2 , and of free methine, CH , may be mentioned. Free methylene was believed to be formed as an intermediate in the photolysis of diazomethane CH_2N_2 and of ketene

⁷ *J. Amer. Chem. Soc.*, 1934, 56, 1311.

⁸ Norrish and Appleyard, *J.C.S.*, 1934, 874.

CH_2CO ,⁹ while methine, CH , is an obvious product of the primary photo-dissociation of acetylene.¹⁰

The first direct proof of the production of free radicals in photochemical reactions was given by Pearson, who modified the Paneth technique for this purpose.¹¹ The apparatus used by Pearson in studying the photolysis of acetone is shown in the diagram below. The acetone was frozen in *I* and the apparatus exhausted. A metal mirror of suitable dimensions was then formed in the quartz tube at *C* by heating the metal (Te, Sb or Pb) in *B*. Acetone vapour at a pressure of the order of 0.5–2.5 mm. was then pumped rapidly through the quartz tube, a small section of which was illuminated by a suitably screened mercury-vapour lamp, as shown. The free radicals formed in the photolysis could then act on the metal mirror at *C*. This was actually found to be eaten away,

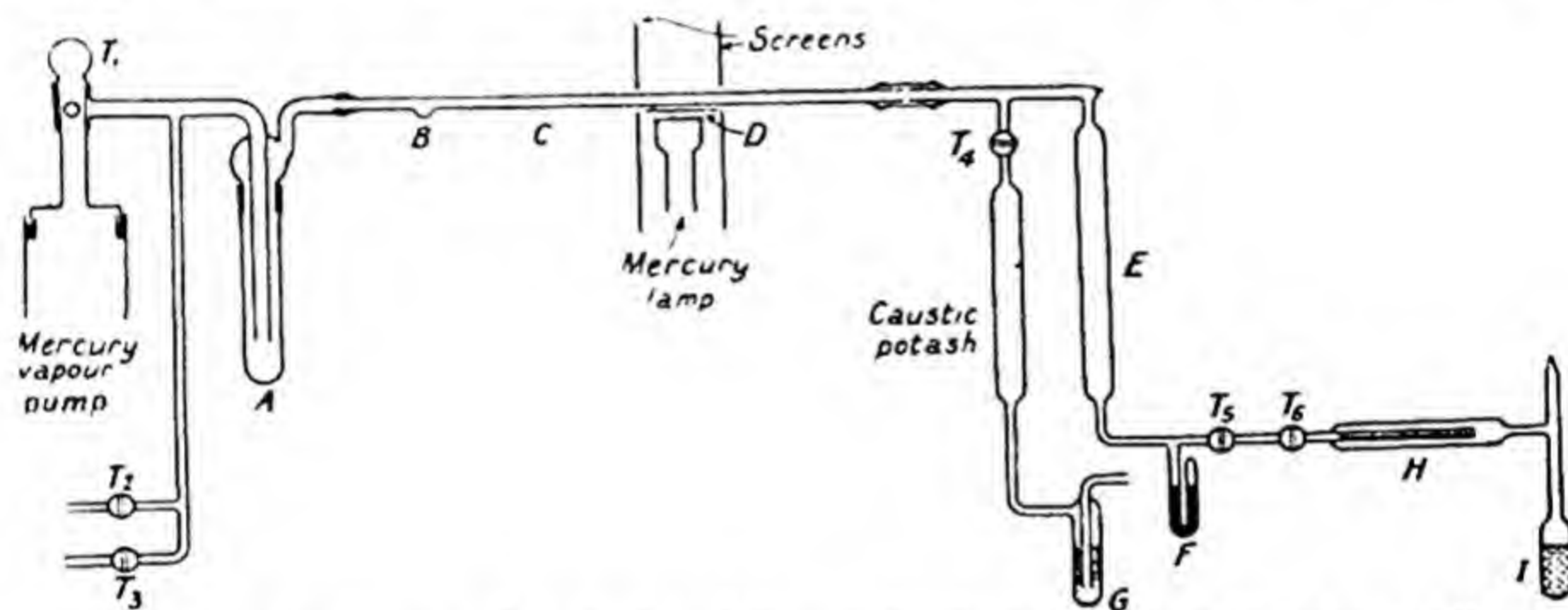


FIG. 49.—Apparatus for study of free radicals produced photochemically.

the time necessary for so doing increasing as the distance of the mirror from the irradiated zone was increased. The volatile products formed by the action of the free radicals on the mirror could be collected in *A*, together with unchanged acetone and products of its photolysis. In the case of the experiments with acetone, dimethyl telluride was identified as formed by the attack of the free radicals on tellurium. Control experiments were, of course, carried out to verify that the attack of the mirror was not due to the undecomposed acetone vapour.

This experimental method also allows the life period of free radicals formed in photolysis to be measured by the usual procedure. This was done by Pearson in the case of the radicals from acetone, and it was shown that the half-life period was of

⁹ Kirkbride and Norrish, *ibid.*, 1933, 119; Norrish, Crone and Saltmarsh, *ibid.*, 1933, 1533.

¹⁰ Norrish, *Trans. Faraday Soc.*, 1934, 30, 111.

¹¹ *J.C.S.*, 1934, 1718.

the order of 5×10^{-3} seconds, a value which is in approximate agreement with that obtained in Paneth's experiments. The same method has been extended with conspicuous success to the study of other radicals, and has proved itself to be of wider applicability than the methods for producing radicals which are based on pyrolysis of either the metal alkyl or of organic compounds. This is because radicals can be produced by photolysis at room temperature, and their chance of survival is accordingly greater.

In an extension of the work on the photolysis of acetone, Pearson and Purcell¹² identified the radicals from dimethyl and diethyl ketones as methyl and ethyl, respectively, by their reactions with mirrors of tellurium, mercury and arsenic. They also proved for the first time that the normal propyl radical exists¹³ by irradiating di-*n*-propyl ketone with ultra-violet light and allowing the radicals formed to react with mercury. The mercury alkyl formed was converted to the mercury alkyl bromide, which was found to be identical with mercury α -propyl bromide. Other work from the same laboratory, making use of the photochemical technique, has resulted in the identification of phenyl, C_6H_5 , benzyl, $C_6H_5CH_2$, tertiary butyl, $C(CH_3)_3$, acetyl, CH_3CO , and benzoyl, C_6H_5CO .

The Ammonium Radical.—There has been much discussion about the existence of the ammonium radical, NH_4 , in the free state. It has been known for a long time that electrolysis of solutions of ammonium salts in water or liquid ammonia with a mercury cathode yields a curious type of 'amalgam'.^{13a} The same product is formed in the interaction between alkali metal amalgams and ammonium salts. These amalgams have the appearance of being puffed up, and are sometimes regarded as froths. It is certain that they contain only mercury, nitrogen, and hydrogen, and that in the spontaneous decomposition the two last-named elements are evolved in the proportions required for the formation of ammonium. The hydrogen formed in the decomposition is nascent. Electrochemical measurements also support the hypothesis that a definite radical such as NH_4 is liberated at the mercury cathode and combines with the mercury, while measurements of the depression of freezing-point of a series of amalgams also support the idea that they consist of solutions of ammonium in mercury. The amalgams formed by alkyl-substituted ammonias are more stable than those from ammonium salts.

The evidence for the transitory existence of ammonium seems fairly convincing, although it is by no means conclusive. The position at the moment is rather similar to the question of the

¹² *J.C.S.*, 1935, 1151.

¹³ *Ibid.*, 1936, 253.

^{13a} Johnston and Ubbelohde, *ibid.*, 1951, 1731.

existence of alkyl radicals when the only experimental evidence was that furnished by the results of electrolysis of fatty acids. It will be necessary, in all probability, to abandon the amalgam method of studying 'ammonium' before much further progress can be made in the study of this substance. At the moment there is no evidence for the transitory existence of the ammonium radical in the gas phase.

Atomic Hydrogen.—Two main methods are available for producing atomic hydrogen in a form which allows it to be studied. The first consists of streaming molecular hydrogen through an electrical discharge at a pressure of the order of 1 mm. of mercury. In the discharge the hydrogen is partially split up into atoms, which survive for a sufficiently long time under certain conditions to be pumped away from the discharge zone and studied. The second method is based on the fact that hydrogen molecules are dissociated into atoms at very high temperatures. Thus a jet of hydrogen directed on to a heated tungsten filament is found to become charged with atomic hydrogen. This method has been developed by Langmuir for welding purposes, and is referred to in greater detail below.

The production of atomic hydrogen in the electric discharge was first described by Wood,¹⁴ who pumped hydrogen through a discharge tube operated from the secondary circuit of a transformer and found that the issuing gas had marked reducing properties, which persisted for some distance from the discharge. The actual distance depended on the rate of pumping, pressure, tube diameter, and nature of the walls. The formation of hydrogen atoms in the discharge is proved by the emission of the line spectrum of hydrogen, as distinct from its band spectrum. The former arises from hydrogen atoms and the latter from hydrogen molecules. The obvious inference is that some of these hydrogen atoms are being carried away from the discharge zone. The reason for their survival is that the process $\text{H} + \text{H} = \text{H}_2$ is exothermic to the extent of 101 kg.cal., so that unless it takes place as a three-body collision, or on the walls of the containing vessel, the newly formed hydrogen molecule will contain at least enough energy for its own dissociation. A third body in the collision, or the proximity of a solid surface, provides a means of disposing of this high energy of recombination and so stabilizing the newly formed molecule. If the energy cannot be disposed of in some such way, then the collision of two hydrogen atoms does not lead to recombination.

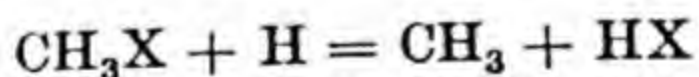
The recombination of hydrogen atoms is catalysed by various substances. If, for example, a piece of platinum foil is mounted

¹⁴ *Phil. Mag.*, 1922, [vi], 44, 538.

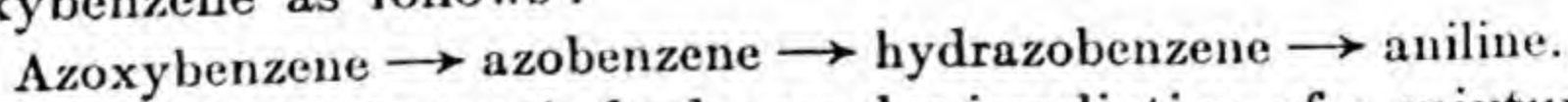
in the gas stream so that the gases leaving the discharge impinge on it, it is rapidly raised to incandescence by the heat liberated in the recombination of hydrogen atoms at the surface. The catalytic activity of the metals decreases in the order Pt, Pd, W, Fe, Cr, Ag, Cu, Pb.¹⁵ The reactions of atomic hydrogen studied up to the present include those with phosphorus, arsenic, and antimony, all of which are converted to their hydrides. Nitrogen is completely indifferent to atomic hydrogen, no ammonia being formed. Sulphur forms hydrogen sulphide readily when placed in the gas streaming away from a hydrogen discharge tube. The rate of reaction may be judged from the fact that in a typical experiment 6 mg. of sulphur were converted to hydride in the course of 5 minutes. Chlorine, bromine and iodine have all been shown to be converted to their hydrides by atomic hydrogen.

Atomic hydrogen has been found by qualitative tests to react with a number of oxides, sulphides and halides of the metals. The oxides and chlorides of copper, lead, bismuth, silver and mercury were reduced readily, for example, while those of aluminium, magnesium, chromium and zinc were not. The sulphides of cadmium and copper were also reduced to the free metal, as were the nitrates and sulphates of lead and copper. Barium sulphate was reduced by atomic hydrogen to barium sulphide. These reactions were carried out without the application of external heat, though a small local temperature rise would be inevitable, owing to recombination of hydrogen atoms at the surface of the material undergoing reduction.¹⁶

Reactions between organic compounds and atomic hydrogen have been extensively studied. With hydrocarbons, hydrogenation, dehydrogenation and disruption of the carbon chain take place simultaneously. With monohalogenated hydrocarbons the primary reaction is probably the formation of a molecule of hydrogen halide, *e.g.*



Other more complex reactions have also been examined. Thus, for example, oleic acid undergoes rapid hydrogenation, while Urey and Lavin¹⁷ have shown that atomic hydrogen is able to reduce azoxybenzene as follows:



The production of atomic hydrogen by irradiation of a mixture of molecular hydrogen and mercury vapour with mercury resonance

¹⁵ Bonhoeffer, *Ergebn. exakt. Naturwiss.*, 1927, 219.

¹⁶ Bonhoeffer, *Z. physikal. Chem.*, 1924, 113, 99; Bonhoeffer and Boehm, *ibid.*, 1926, 119, 385.

¹⁷ *J. Amer. Chem. Soc.*, 1929, 51, 3286.

radiation of wave-length 2537 Å. has been extensively studied in connexion with such problems as the photochemical polymerization of hydrocarbons, but a full discussion of the more physical aspects of such work cannot be given here.¹⁸

Langmuir's method of producing atomic hydrogen by means of thermal dissociation of molecular hydrogen¹⁹ is perhaps the only direct technical application of atomic gases to be made up to the present, and may therefore be described in some detail. The principle employed is to blow a current of hydrogen across an arc (20 amp. at 300–800 volts) struck between tungsten electrodes in an atmosphere of hydrogen. The degree of dissociation of the hydrogen may be calculated, and is found to be 9.03 per cent at 3000° and 94.7 per cent at 5000°. When this stream of gas containing atomic hydrogen is directed on to a metal surface placed at a few centimetres from the arc, intense local heating occurs, due to catalytic recombination of the atoms. It has been found possible to use this heating effect to melt some of the most refractory materials. Thus tungsten, tantalum, and thorium oxide have all been melted by this process. It has the great advantage in welding operations to which it has been applied that the hydrogen furnishes a protective atmosphere, so that deterioration of the weld by oxidation is minimized.

Pietsch has studied the reactions between atomic hydrogen and certain metals, using the apparatus shown diagrammatically below.²⁰ The metals examined were mounted in the bulb tube, shown on the right of the discharge tube, so as to expose them to the action of atomic hydrogen. It was found that silver foil became covered with a white film in the course of 2 hours' exposure. The product when treated with water gave silver hydroxide and evolved a gas which was taken to be hydrogen. Powdered silver at 250–350° gave a white product, which was probably a silver hydride mixed with unchanged silver, and for which the hydrogen dissociation pressure varied from 3.5×10^{-2} mm. at 289° to 72 mm. at 1173°. In the course of such an experiment the metal studied becomes hot because of reaction and recombination at its surface, but the amount of heating can be controlled by altering the discharge conditions and pressure so as to modify the concentration of hydrogen atoms in the gas stream. Copper and gold gave similar results to silver, although the hydrides formed were much more readily decomposed by heat, and a lower concentration of atomic hydrogen had to be employed

¹⁸ See *Grundlagen der Photochemie*, by K. F. Bonhoeffer and P. Harteck (Theodor Steinkopff, 1933).

¹⁹ Cf. *General Electric Review*, 1926, 29, 153.

²⁰ *Z. Elektrochem.*, 1933, 39, 577.

to avoid overheating of the metal. Beryllium was also found to be attacked. Gallium became covered with a film of hydride at $100\text{--}170^\circ$, and in the case of indium a reaction between the vapour of the element and atomic hydrogen took place. A blue luminescence was observed and a grey-white hydride could be frozen out from the gas stream. It decomposed on warming, leaving a deposit of indium on the glass. Metallic tantalum was transformed by atomic hydrogen into a brittle substance which had a definite dissociation pressure of hydrogen over it. In assessing the importance of this preparative work it must be remembered that although definite compounds were not isolated and analysed, the observa-

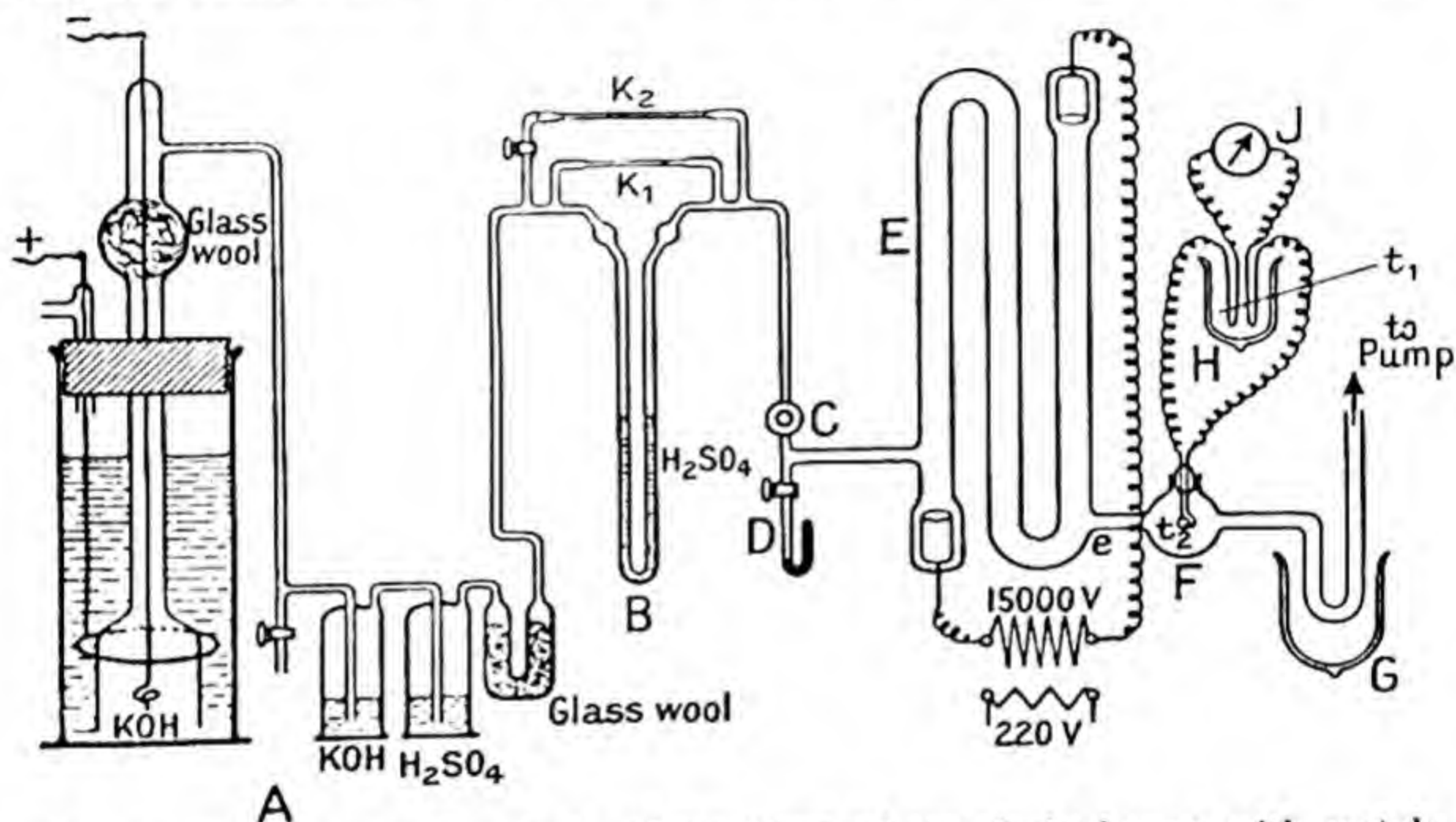


FIG. 50.—Apparatus for study of reactions of atomic hydrogen with metals.

tions were made with small quantities of material. Undoubtedly atomic hydrogen can form hydrides which are not formed directly. This is the case, for example, with silver, beryllium, gallium and indium. Pietsch expresses the view that the hydrides formed by the atomic hydrogen are salt-like, but this is not necessarily true. Thus in the case of tantalum, for example, the formation of an interstitial compound would seem to be equally likely.

A hydride of mercury has also been prepared from atomic hydrogen and mercury vapour.²¹ Mercury vapour was injected through a jacketed tube into a hydrogen stream carrying atomic hydrogen, the mixing zone being cooled in liquid air. A black product separated out on the cooled surface, but it decomposed into mercury and hydrogen at -125° to -100° . From the

²¹ Geib and Hartek, *Ber.*, 1932, 65, 1550.

quantities of hydrogen evolved and of mercury remaining it was concluded that the deposit consisted of 70 per cent of a hydride HgH and 30 per cent of metallic mercury.

Several other interesting addition reactions of atomic hydrogen taking place at low temperatures have been described. These addition reactions probably occur more readily at low temperatures because the kinetic energy of the reactants is less. Hydrogen atoms, produced separately in the electrical discharge, and mixed with molecular oxygen at the temperature of liquid hydrogen, give a quantitative yield of hydrogen peroxide.²² This is not, however, the ordinary form of hydrogen peroxide, for on warming to -80° a vigorous exothermic reaction, accompanied by partial decomposition into water and oxygen, takes place, and ordinary hydrogen peroxide remains.

Nitric oxide and hydrogen atoms react at the temperature of liquid air to form an explosive substance of the composition $(\text{HNO})_n$.²³ This separates as a bright yellow deposit at liquid air temperature, as much as 250 mg. having been prepared, and it resembles the product obtained by the action of atomic oxygen on ammonia. The deposit becomes white in colour on raising the temperature and a change sets in at -95° , with some decomposition into nitrous oxide and traces of hydrogen and nitric oxide. The substance was analysed by decomposing the vapour with a glowing platinum spiral and a ratio $\text{H}:\text{N}:\text{O} = 1:1:1$ was found. It was thought that the low temperature product was an addition compound, but that at -95° this yielded hyponitrous acid, $\text{H}_2\text{N}_2\text{O}_2$, and nitramide, NH_2NO_2 , both of which were detected by qualitative tests. This low temperature change at -95° was accompanied by a small amount of decomposition into the products mentioned above.

Hydrogen atoms react with hydrogen cyanide at low temperatures forming a substance with the formula H_3CN , which decomposes when slowly heated, yielding ammonia, methylamine and various condensation products. Sulphur dioxide also forms an addition product of the formula $\text{H}_2\text{S}_2\text{O}_2$, which decomposes when the temperature is raised, forming SO_2 and H_2S .²⁴

Harteck has described a method of obtaining atomic hydrogen, oxygen and nitrogen at gas pressures up to 20 mm.²⁵ The principle employed is to circulate a gas mixture containing a partial pressure of 15–20 mm. of neon and a hydrogen pressure of the order of

²² Geib and Harteck, *Ber.*, 1932, 65, 1551.

²³ Harteck, *ibid.*, 1933, 66, 423.

²⁴ Geib and Harteck, *Trans. Faraday Soc.*, 1934, 30, 131.

²⁵ Harteck, *Z. Elektrochem.*, 1936, 42, 536.

0.3 mm. The inert gas makes it possible to operate the discharge at a much higher pressure than would otherwise be possible, while the dissociation of hydrogen into atoms by the discharge proceeds quite normally. The method has the special advantage that it enables the gas stream containing hydrogen atoms to be bubbled through liquids and solutions. It has been found in this way that solutions of silver sulphate or nitrate are reduced to metallic silver. Cupric chloride yields copper and hydrochloric acid, mercuric chloride yields mercurous chloride and hydrochloric acid, and hydrogen peroxide is transformed into water.

Atomic Oxygen.—Atomic oxygen may be produced by streaming molecular oxygen at a pressure of about 1 mm. through an electrical discharge. The apparatus is very similar to that used in studying atomic hydrogen, and the gas passing away from the discharge consists of a mixture of molecular and atomic oxygen.²⁶ The recombination of the atoms is catalysed by various substances, and a metal such as platinum may be melted by the heat of recombination when it is placed in the gas passing away from a discharge. The actual time of survival of atoms depends on the diameter of the tube through which the gases are passing, the nature of its walls, the presence of inert gases, and the oxygen pressure.

An alternative method of producing atomic oxygen is by irradiation with light of wave-length falling within the region of continuous absorption of oxygen, *i.e.* of wave-length less than 1900 Å. Such light may be obtained by passing a condensed spark between aluminium electrodes in air. Alternatively a special type of xenon discharge lamp may be employed.²⁷ This lamp emits the xenon resonance lines at 1495 Å. and 1295 Å., these wave-lengths corresponding to energies of 193 and 219 kg.cal., respectively. In either case dissociation of oxygen molecules into atoms results.

Atoms of oxygen are almost certainly produced in an ordinary ozonizer as an intermediate in the production of ozone. The recombination of two atoms to form an oxygen molecule and the combination of an atom and a molecule to form ozone can occur only as three-body collisions or on a solid surface, and Kistiakowsky²⁸ has shown that in ozone formation the efficiencies of various molecules as partners in such three-body collisions for the formation of ozone have the following relative values:

O_2	CO_2	CO	N_2	A
1	0.8	0.62	0.28	0.13

The energy of activation of the process $O + O_2 = O_3$ is only

²⁶ Harteck and Kopsch, *Z. physikal. Chem.*, 1931, B, 12, 327.

²⁷ Groth, *Z. Elektrochem.*, 1936, 42, 533.

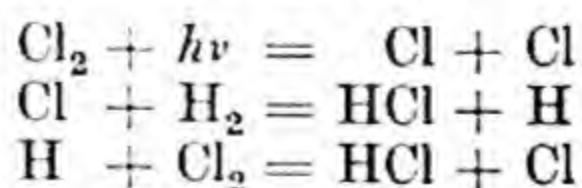
²⁸ *Z. physikal. Chem.*, 1925, 117, 337.

4 kg.cal., and the reaction of oxygen atoms produced in a discharge with molecular oxygen at low temperatures is a convenient method of preparing high concentrations of ozone. Accidental production of liquid ozone from the reaction is also a potential source of dangerous explosions in work on atomic oxygen in which the discharge tube is employed.

The reactions of atomic oxygen have been extensively studied.²⁹ With hydrogen, as might be expected, water is the ultimate product, although there is some uncertainty as to the mechanism of its formation. Hydrogen sulphide and carbon disulphide both react at low pressure with a blue luminescence, and the production of S, SO₂, SO₃, H₂SO₄, H₂O, CO and CO₂. The reaction of oxygen atoms with carbon monoxide is very slow at room temperature. Hydrogen chloride and hydrogen bromide are decomposed with production of the free halogens. All hydrocarbons are attacked more or less slowly, the reaction being accompanied by luminescence, the spectrum of which shows OH, CH and sometimes also CC bands.

Addition reactions, similar to those for atomic hydrogen, may also be observed with atomic oxygen at low temperatures. Thus acetylene gives a substance the composition of which approximates to C₂H₂O₂ and which decomposes at temperatures above - 90°, giving mainly water, formic acid and glyoxal. Benzene adds on three oxygen atoms per molecule at - 80°, but the substance formed decomposes at higher temperatures. Ammonia reacts with oxygen atoms, giving an explosive substance which is probably HNO or NH₃O. There are still many possible extensions of this field of investigation. Among the most promising is the use of a relatively high pressure of a rare gas as a carrier for atomic oxygen, using the same general method as has been described for hydrogen atoms. This would facilitate the study of reactions between oxygen atoms and liquids.

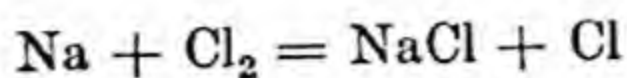
Atomic Chlorine and Bromine.—The existence of free chlorine atoms as intermediates in chemical reactions has been recognized for many years, particularly in the case of the photochemical combination of hydrogen and chlorine, for which Nernst has proposed the following chain reaction:



The chlorine atoms are produced in this instance by the photochemical dissociation of chlorine, and as the reaction proceeds

²⁹ Cf. Geib, *Ergebn. exakt. Naturwiss.*, 1935, 44.

there will be a small but definite concentration of atoms present in the reacting mixture. The thermal reaction of sodium vapour and chlorine is similar, and is believed to take place *via* the initial stage :



If hydrogen or methane is added to the reacting mixture in the dark, the formation of hydrogen chloride or of methyl chloride can be observed at temperatures lower than those needed for direct thermal chlorination, which is again indirect proof that chlorine atoms are present. These methods are not, however, suitable for studying the reactions of atomic chlorine. Even when chlorine is irradiated with a wave-length capable of dissociating the gas into atoms (*i.e.* $\lambda < \text{circa } 4785 \text{ \AA.}$), the atoms recombine very rapidly, and none of them survive for a sufficient time for their reactions to be studied unless low pressures and wide reaction vessels are used. The use of low pressures would minimize recombination by three-body collisions in the gas phase, while the fact that the reaction vessel used was large would ensure that the rate of recombination of chlorine atoms on the walls was small.

The production of atomic chlorine in a discharge was first carried out successfully by Rodebush and Klingelhoefer,³⁰ use being made of an electrodeless discharge in streaming chlorine at a pressure of less than 1 mm. The catalytic behaviour of various materials in promoting the recombination of chlorine atoms was studied by coating them in turn on to the bulb of a thermometer which was placed in the gases streaming away from the discharge, and observing the rise in temperature. Silver and copper were good catalysts, but were also rapidly attacked with formation of adherent layers of their chlorides. Nickel and gas carbon also had a good catalytic action, while recombination on surfaces of glass, sodium chloride, potassium chloride and platinum was small. It was also shown that chlorine mixed with chlorine atoms, when introduced into hydrogen in the dark, reacted rapidly to form hydrogen chloride. This experiment gives a direct verification of the Nernst mechanism for the photochemical reaction of hydrogen and chlorine.

Schwab and Friess³¹ employed a glow discharge in chlorine at a pressure of < 1 mm. to produce chlorine atoms. In much the same way as for the production of atomic hydrogen, chlorine was streamed rapidly through a quartz discharge tube, 23 mm. wide and 230 cm. long, fitted with water-cooled iron electrodes. As it left the discharge tube the chlorine contained a small concentration

³⁰ *J. Amer. Chem. Soc.*, 1933, 55, 130.

³¹ *Z. Elektrochem.*, 1933, 39, 586.

of atoms which diminished as the distance from the discharge increased, due to recombination in the gas phase and on the walls. The spectrum of the discharge showed the line spectrum of chlorine, thus proving that atoms were present. The actual streaming velocity of the chlorine through the discharge was about 400 cm. per sec., and the time for the activity of the chlorine to fall to half its value was about 3×10^{-3} seconds. The relative concentration of atoms present at any point could be measured by the rise in temperature indicated by a thermo-junction inserted in the gas stream.

The chemical reactions of atomic chlorine were not extensively studied. It was shown, however, that sulphur and red phosphorus reacted slowly with the chlorine-atomic chlorine mixture. Copper and chromium trioxide reacted more rapidly, and metallic tin was vigorously attacked, with a considerable rise in temperature. Atomic chlorine also reacted with methane, chloroform, and with carbon monoxide.

Experiments with atomic bromine have been carried out by Schwab.³² The technique used was very similar to that in the study of chlorine atoms, and consisted in pumping a stream of bromine vapour through an electrical discharge at a pressure of 0.1 mm. The line spectrum of bromine was observed in the discharge, showing that atoms of bromine were present, and it was estimated that from 10 to 40 per cent of the bromine in the discharge zone was in the atomic form. Further study of the reactions of atomic bromine was, however, prevented by the fact that bromine atoms were found to recombine on the walls at every collision, to re-form molecular bromine. It was therefore impossible to remove the gas containing the free atoms away from the discharge zone, and carry out experiments with appreciable atom concentrations similar to those already described in the cases of atomic hydrogen, oxygen and chlorine.

Other Short-Lived Radicals.—A number of other free radicals exist under conditions which so far have not permitted a detailed study of their properties to be carried out. Of these the most interesting is perhaps the hydroxyl radical, OH, which has long been associated with the series of emission bands, the strongest of which is situated at *circa* 3064 Å., in the spectrum of an electrical discharge through water vapour, and in that of the flames of hydrogen and its compounds burning in air or oxygen. The hydroxyl radical is also formed in the thermal dissociation of water vapour at temperatures above about 1000°. Bonhoeffer and Reichardt³³ have studied the ultra-violet absorption spectrum

³² *Z. physikal. Chem.*, 1934, B, 27, 452.

³³ *Ibid.*, 1928, 139, 75.

of water vapour heated to temperatures between 1000° and 1600° and have observed the OH bands in absorption under these conditions. The partial pressure of free hydroxyl in their experiments was 8 mm. of mercury at 1600° and 0.3 mm. of mercury at 1150° .

The production of free hydroxyl radicals in the electrical discharge through water vapour is indicated by the emission of the OH bands, and has been verified by Oldenberg³⁴ by photographing the absorption spectrum of the gas in such a discharge tube immediately after the discharge had been switched off. The OH radicals could be detected by their absorption spectrum for as long as 0.4 second after interrupting the discharge. This observation demonstrates that they have a life period which is much the same as that of atomic hydrogen, and suggests that it should be possible to study their reactions by streaming water vapour at a high rate through an electrical discharge at low pressure.

Urey and Lavin have attempted to study the chemical reactions of free hydroxyl radicals produced by passing a discharge through water vapour, using the same technique as for the study of atomic hydrogen.³⁵ They concluded that the gas issuing from the discharge tube was more reactive than atomic hydrogen, although the latter was undoubtedly present. When mixed with ethylene, for example, the gas gave a trace of acetaldehyde. In later work Lavin and Stewart³⁶ found that there was an approximate proportionality between the amount of hydrogen peroxide formed in passing water vapour through a discharge and the intensity of the OH emission bands in the discharge zone.

One of the major difficulties in the study of the free hydroxyl radical is that one cannot obtain it without the simultaneous presence of other radicals. When produced from water vapour it is admixed with atomic hydrogen, and Rodebush³⁷ has shown that even if free from other products initially, the hydroxyls could undergo a surface reaction $\text{OH} + \text{OH} = \text{H}_2\text{O} + \text{O}$, leading to formation of atomic oxygen.

Free imine, NH, is a radical which is associated with emission bands in the spectrum of a discharge through ammonia or nitrogen-hydrogen mixtures at low pressures. The information about the chemical reactions of this substance is, however, singularly incomplete. Lavin and Bates produced the radical by passing ammonia through a discharge tube at low pressure.³⁸ Addition of ethylene

³⁴ *J. Phys. Chem.*, 1937, **41**, 293.

³⁵ *J. Amer. Chem. Soc.*, 1929, **51**, 3290.

³⁶ *Proc. Nat. Acad. Sci.*, 1929, **15**, 829.

³⁷ *J. Phys. Chem.*, 1937, **41**, 283.

³⁸ *Proc. Nat. Acad. Sci.*, 1930, **16**, 804.

to the gas passing away from the discharge gave rise to a yellow luminescence, and a white solid was deposited which gradually changed to an oil and then to a black solid. Oxygen produced a blue-green luminescence when added to the gas stream, and the formation of oxides of nitrogen could be detected. Fragments of metal placed in the gas stream destroyed the active material, but a plug of zinc and chromic oxides, which is able to cause hydrogen atoms to recombine, had no effect on the gases from the ammonia discharge. Presumably, therefore, the activity is not associated with the presence of atomic hydrogen, and it may well be that the imine radical is the active agent. This problem is one in which it should be possible to supplement the existing experimental evidence, and so place the imine radical on a sure basis.

Active Nitrogen.—Active nitrogen is produced by passing a condensed electric discharge from an induction coil, with a spark-gap in series in the circuit of its secondary, through nitrogen at a pressure of less than 1 mm. Alternatively a high frequency electrodeless discharge can be passed through the nitrogen. In either case it is found that when the discharge is switched off the gas in and near the discharge zone continues to emit a feeble yellowish luminescence for some time. If nitrogen is being streamed through the discharge, then the gas passing away from the discharge zone emits the yellow glow. Its persistence is governed entirely by the conditions (pressure, temperature, foreign gases present, and nature of the walls of the containing vessel), but in large bulbs coated on the inside with metaphosphoric acid, the glow has been found to persist for six hours or more.³⁹ Naturally, it becomes exceedingly feeble towards the end of this time.

This glowing nitrogen is found to be endowed with abnormal chemical activity and is called active nitrogen. Whether this active form of nitrogen can correctly be called a free radical of short life is doubtful, but it is certainly sufficiently akin in its reactivity to substances such as atomic hydrogen or free alkyl radicals to justify its description in this chapter. The first systematic observations on active nitrogen were made by Lord Rayleigh (then the Hon. R. J. Strutt).⁴⁰ The apparatus employed is shown in Fig. 51. Nitrogen was purified in the bulb *A* by heating at 300° with a liquid sodium-potassium alloy *B*, and was admitted to the discharge tube by the fine-adjustment stopcock *F*. The effect of adding oxygen to the nitrogen could be examined by means of the fine capillary *H*. The discharge was located at *E* between the two platinum electrodes, and observations on the chemical reactions

³⁹ Rayleigh, *Proc. Roy. Soc.*, 1935, A, 151, 567.

⁴⁰ Rayleigh, *ibid.*, 1911, A, 85, 219.

of the active nitrogen could be made in the bulb *J*, which could be modified to suit the particular aspect of the problem being studied. The manometer *G* served to indicate the pressure in the apparatus. This could be adjusted by altering the setting of the stopcock *F*.

The chemical reactions of active nitrogen were for the most part studied qualitatively. With yellow phosphorus a nitride was formed together with a certain amount of red phosphorus. Arsenic gave a nitride, which could be detected by boiling with sodium hydroxide solution, when ammonia was evolved. With sulphur chloride, hydrogen sulphide, or carbon disulphide a blue solid was formed which was taken to be sulphur nitride $(\text{NS})_x$, while carbon disulphide formed a brown solid, believed to be polymerized carbon monosulphide, in addition to nitrogen sulphide. Certain metals were transformed by active nitrogen into their nitrides; thus mercury, zinc, cadmium, and sodium all gave nitrides, to which qualitative

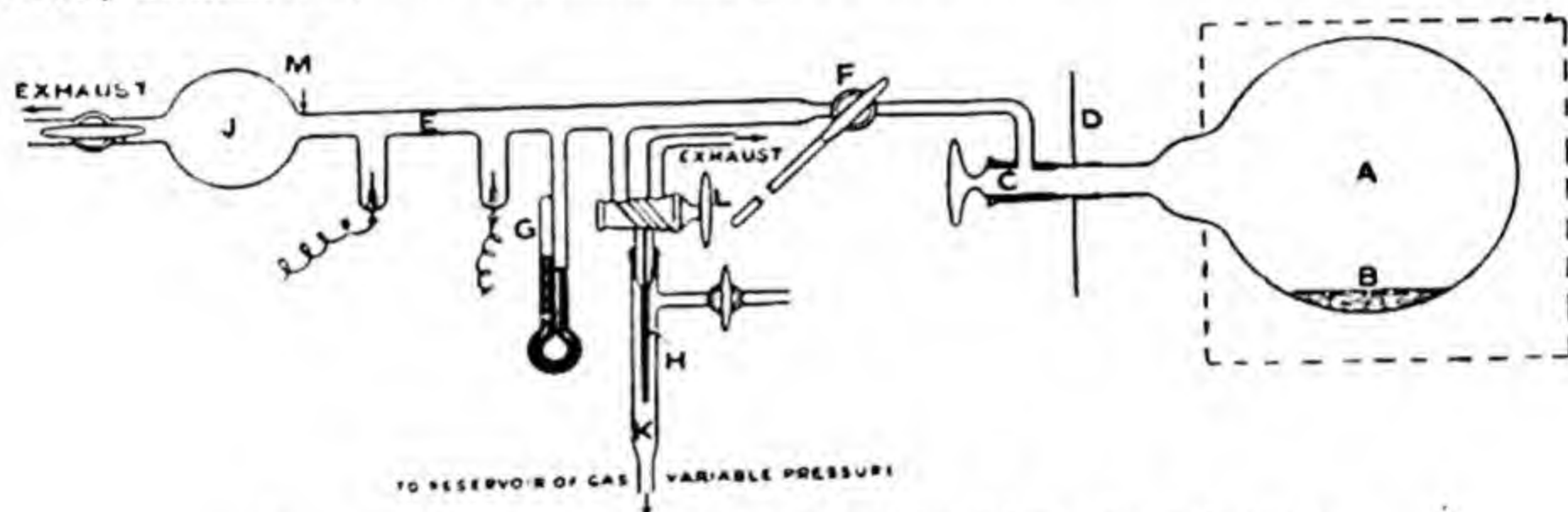


FIG. 51.—Apparatus for production of active nitrogen.

tests were applied. Active nitrogen reacted with nitric oxide, forming nitrogen peroxide and nitrogen. The absorption of active nitrogen by phosphorus was used by Strutt in measuring the concentration of active nitrogen in the gas passing away from the discharge tube, and a value of about 0.5 per cent was obtained. The precise figure naturally depends on the experimental conditions employed.

Willey observed that the glow of active nitrogen was destroyed catalytically by metals such as platinum, iron, and silver.⁴¹ In studying the reactions of active nitrogen with certain gases, Willey and Rideal observed that reactions could take place which required about 50,000 g.cal. per g.mol. to bring them about. Hydrogen iodide, for example, was decomposed readily. The critical increment for its decomposition is 45,700 g.cal. Hydrogen bromide (crit. increment 50,000 g.cal.) was decomposed less readily, and hydrogen chloride (crit. increment 90,000 g.cal.) was unaffected

⁴¹ *J.C.S.*, 1927, 2188.

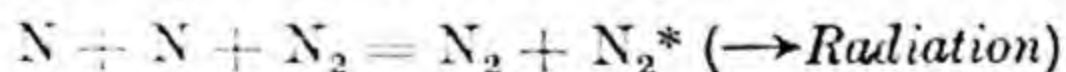
by active nitrogen. This affords a measure of the energy available in the active gas.

The activity of active nitrogen was not confined to the initiation of chemical reactions, however, for it was also capable of exciting spectra without any chemical change taking place. Thus, for example, admixture with iodine vapour gave a beautiful blue luminescence, and with the vapour of mercury or tin halides the band spectra of the molecules of HgCl and SnCl were excited. In these cases there was no chemical reaction. With sodium, on the other hand, formation of the nitride was accompanied by the excitation of the line spectrum of the metal, and with many carbon compounds the cyanogen bands were excited. Yet other substances functioned purely as diluents to the glow, among these being hydrogen and carbon dioxide.

The production of active nitrogen is catalysed by the presence of amounts of the order of 0.1 per cent of impurities such as oxygen or methane, but it has been established that the afterglow can also be observed in chemically pure nitrogen.⁴² The glow associated with active nitrogen can be destroyed by heating to 300° . Active nitrogen is found to be electrically conducting, *i.e.* it contains ions. This, however, has been shown to be a secondary effect associated with the insertion of electrodes into the gas stream, and it is almost certain that charged particles play no part in the chemical reactions of the active gas.⁴³

The nature of active nitrogen has been the subject of much discussion. The yellow glow shows a band spectrum which consists of a selection of the bands of the first positive group of nitrogen. The intensity of bands in the red, yellow and green is considerably enhanced. The spectrum is due to the emission of light from excited N_2 molecules.

Strutt supposed that the luminosity represented the emission of the energy of recombination of two nitrogen atoms in a bimolecular reaction.⁴⁴ Later Sponer⁴⁵ suggested that the luminosity arises from the chemiluminescent recombination of two nitrogen atoms in presence of a nitrogen molecule. Thus



The molecule N_2^* is the energy-rich molecule from which radiation takes place. In essence this is the explanation which is now generally accepted, although some modification of Sponer's theory has been necessary on account of the fact that the energy of

⁴² Baker and Strutt, *Ber.*, 1914, **47**, 2283.

⁴³ Willey and Springfellow, *J.C.S.*, 1932, 142.

⁴⁴ *Proc. Roy. Soc.*, 1912, **A**, 86, 263.

⁴⁵ *Z. Physik.*, 1925, **34**, 622.

recombination of nitrogen atoms was insufficient to account for some of the features of the spectrum of the afterglow.⁴⁶

In summarizing the present position of the problems presented to the chemist by active nitrogen, one is compelled to admit that the question of the origin of the luminescence has not been satisfactorily settled. The systematic investigation of the chemical reactions of the active gas is, moreover, very incomplete. Such facts as we have are indeed based largely on qualitative evidence. With regard to the nature of active nitrogen, we still have no conclusive evidence. It seems probable, however, that the chemically reactive gas contains metastable nitrogen atoms and also metastable energy-rich molecules. The bulk of evidence is against the existence of a reactive molecule N_3 , analogous to ozone. Willey⁴⁷ has shown that nitrogen can be chemically active and yet show no visible glow, a fact which lends support to the view that the luminescence of active nitrogen is a secondary effect arising from the high energy imparted to the nitrogen by the electrical discharge.

⁴⁶ For a full discussion of the physical aspects of this subject, see *Collisions of the Second Kind. Their Role in Physics and Chemistry*, by E. J. B. Willey. Edward Arnold, 1937.

⁴⁷ *J.C.S.*, 1927, 2831.

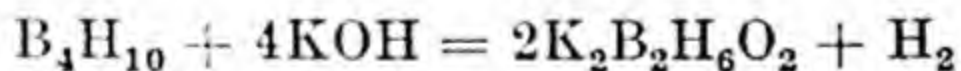
CHAPTER X

NON-METALLIC OXIDES AND RELATED COMPOUNDS

Oxides and Oxyacids of Boron.

In addition to the well-known compound boron trioxide and the acids derived from it, several suboxides and acids with reducing properties have been described. Thus an unstable oxide with the empirical formula BO is formed in the reaction between boron and zirconium dioxide at 1800°. ¹ This is probably similar in type to the oxide SiO, which is obtained by the high temperature reduction of silica. ² In neither case has the chemistry been studied in any detail.

Two other suboxides, B₂O₂ and B₄O₅, have been described, ³ though their characterization is far from complete. Both may be regarded as derivatives of the hydrolysis products of magnesium boride, Mg₃B₂. During the hydrolysis with water, hydrogen is evolved and two acidic substances formed. The first, H₁₂B₄O₆, has been isolated as the ammonium salt (NH₄)₂B₄H₁₀O₆ and when heated gives first H₂B₄O₆ and then B₄O₅. The second, H₂B₂H₄O₂, which has been isolated as the potassium salt K₂B₂H₄O₂, gives the oxide B₂O₂. The existence of these two suboxides has not yet been adequately confirmed, though there is no doubt that compounds with reducing properties are formed both in the hydrolysis of magnesium boride and in the reaction of boron hydrides with water or alkalis. Stock, for example, describes a potassium hypoborate K₂B₂H₆O₂ obtained in the reaction of B₄H₁₀ with KOH,



The corresponding sodium, rubidium and caesium salts were also prepared and the same salt was obtained in the reaction of diborane with either solid or aqueous alkali. These salts have very strong reducing properties.

¹ Zintl, Morawietz and Gasting, *Z. anorg. Chem.*, 1940, 245, 8.

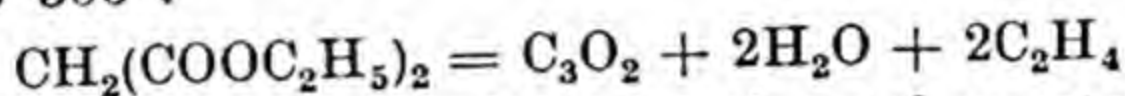
² Zintl, *ibid.*, 1940, 245, 1.

³ Travers and Ray, *Proc. Roy. Soc.*, 1913, 87, 163. Ray, *J.C.S.*, 1914, 2162; 1918, 803; 1922, 1088. Ray, *Quart. J. Indian. Chem. Soc.*, 1924, 1, 125. See also Wiberg, *Z. anorg. Chem.*, 1930, 191, 49; Stock, *Hydrides of Boron and Silicon*, 1933.

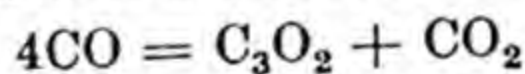
Hydrolysis of the boron subchloride B_2Cl_4 occurs without evolution of hydrogen, and yields a solution with reducing properties which are attributed to the acid $B_2(OH)_4$.⁴ The methyl ester $B_2(OCH_3)_4$ was prepared by treating the chloride $B(OCH_3)_2Cl$ with sodium amalgam and on hydrolysis gave the free acid as a white solid which was soluble in water.

Carbon Suboxide.

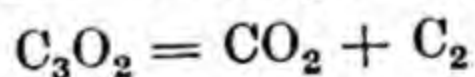
Carbon suboxide, C_3O_2 , is a gas at room temperature. It boils at 6° and has a melting-point of -111.3° . It has a pungent odour and is toxic. Several early investigators prepared what they believed to be suboxides of carbon,⁵ but the substance C_3O_2 was first identified by Diels and Wolf,⁶ who obtained it by heating a mixture of diethyl malonate with a large excess of phosphorus pentoxide to 300° .



The suboxide is also formed by heating other esters of malonic acid or malonic acid itself with phosphorus pentoxide, and is readily separated in a state of purity by fractionation. Low yields are usually obtained, this being due in part at least to the readiness with which the oxide polymerizes on heating. Various other methods of preparing the suboxide are available.⁷ The pyrogenic decomposition of diacetyltartaric anhydride gives a moderate yield, while it has been reported that carbon monoxide is decomposed in an ozonizer into the suboxide and carbon dioxide.⁸



The action of heat on carbon suboxide produces two reactions, one a polymerization and the second a decomposition. The decomposition reaction at 200° takes place according to the equation



The initial products of this reaction are carbon dioxide and a gaseous substance which Klemenc, Wechsberg and Wagner termed di-carbon.⁹ The absorption spectrum of carbon suboxide undergoing decomposition at 200° was photographed and the Swan bands of carbon were observed. These bands in an absorption spectrum are definitely associated with absorption of light by the molecule C_2 in the gaseous phase. Further evidence for the above mode of decomposition of the suboxide was furnished by the formation of carbon dioxide, but not of carbon monoxide, in the decomposition

⁴ Stock, Brandt and Fischer, *Ber.*, 1925, 58, 643.

⁵ Cf. Reyerson and Kobe, *Chem. Reviews*, 1930, 7, 479.

⁶ *Ber.*, 1906, 39, 689.

⁸ Ott, *Ber.*, 1925, 58, 772.

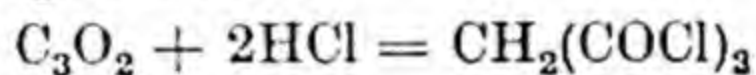
⁷ Reyerson and Kobe, *loc. cit.*

⁹ *Z. physikal. Chem.*, 1934, A, 170, 97.

of the suboxide (provided oxygen was excluded). Moreover, a solid deposit of graphite formed in the heated vessel in which the decomposition was taking place.

Gaseous carbon suboxide is relatively stable when kept in dry glass apparatus at room temperature. It polymerizes rapidly on heating, however, and the presence of the polymeric form catalyses the polymerization at room temperature. Liquid carbon suboxide polymerizes readily to a dark red solid which is soluble in water.¹⁰ On heating this polymer to 37° it loses carbon dioxide and forms a solid product which is only partially soluble in water. It may be noted in this connexion that carbon subsulphide, which is the sulphur analogue of the suboxide, and which is obtained by passing carbon disulphide through a glass tube heated to 600°, also polymerizes to a solid when heated to 120°.

The chemical reactions of gaseous carbon suboxide are of considerable interest. Thus the oxide will explode when mixed with oxygen and ignited, carbon dioxide being produced. It yields malonic acid when treated with cold water, while with ammonia it forms malonamide, $\text{CH}_2(\text{CONH}_2)_2$. With dry hydrogen chloride malonyl chloride is produced.



The reactions with numerous organic compounds have also been investigated.

There is little doubt as to the constitution of this oxide. Its vapour density and molecular weight are in accord with the formula C_3O_2 . Quite recently bond distances in the gas state have been studied by the methods of electron diffraction and it has been found that the C—O and C—C distances are 1.18–1.20 and 1.27–1.30 Å., respectively.¹¹ The molecule is linear ($\text{O}=\text{C}=\text{C}=\text{C}=\text{O}$), but if the bonds were ordinary double bonds the interatomic distances would be 1.28 and 1.33 Å., respectively. This discrepancy has been interpreted as arising from resonance in the molecule of the suboxide.

Pentacarbon dioxide, C_5O_2 , the formation of which in very low yield as a secondary product of the polymerization of C_3O_2 at 200° was claimed by Klemenc and Wagner,¹² is described as a relatively stable substance. Its boiling-point was given as $105 \pm 3^\circ$. The existence of this oxide was denied by Diels¹³ and has not been confirmed by any other worker. It is noteworthy that its formation

¹⁰ Diels and Wolf, *Ber.*, 1906, 39, 689.

¹¹ Boersch, *Monatshefte*, 1935, 65, 311; Pauling and Brockway, *Proc. Nat. Acad. Sci.*, 1933, 19, 860. See also Thompson and Healey, *Proc. Roy. Soc.*, 1936, 157, 331; Thompson, *Trans. Faraday Soc.*, 1941, 37, 249; Lord and Wright, *J. Chem. Physics*, 1937, 5, 642.

¹² *Ber.*, 1937, 70, 1880.

¹³ *Ibid.*, 1938, 71, 1197.

was observed by Klemenc and Wagner only with carbon suboxide prepared by the decomposition of malonic acid: more than two hundred experiments made with suboxide prepared from diacetyl tartaric acid gave no trace of pentacarbon dioxide. This suggests that the supposed new oxide may in reality have been an impurity produced in preparing the suboxide, though it is impossible at present to arrive at a final conclusion on this point.

Oxides of Nitrogen.

The formulæ of the oxides and oxyacids of nitrogen known at present are as follows:

N_2O	$\text{H}_2\text{N}_2\text{O}_2$	Hyponitrous acid
NO	HNO_2	Nitrous acid
N_2O_3	HNO_3	Nitric acid
$\text{NO}_2(\text{N}_2\text{O}_4)$	HNO_4	Pernitric acid
N_2O_5		
NO_3		

Nitrous oxide has a linear molecule,¹⁴ the bond lengths in which are accounted for by postulating resonance between the structures $-\ddot{\text{N}}=\ddot{\text{N}}^+=\ddot{\text{O}}:$ and $:\text{N}\equiv\ddot{\text{N}}^+-\ddot{\text{O}}:-$. Although it is formed in the decomposition of hyponitrous acid, it does not function as an anhydride in the sense of forming the acid or its salts on treatment with water or alkali.

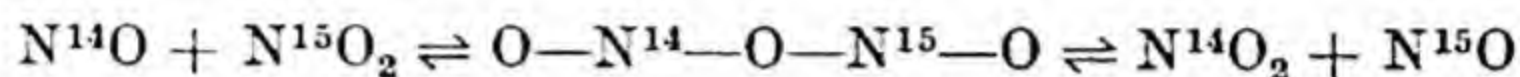
Nitric oxide is a molecule with an odd number of electrons and is paramagnetic. The N—O interatomic distance is 1.14 Å., which is intermediate between the values for the structure $\text{N}=\text{O}$ (1.18 Å.) and $\text{N}\equiv\text{O}$ (1.06 Å.). The structure may be represented as $:\text{N}\equiv\text{O}:$, or as a resonance hybrid between the forms $+\ddot{\text{N}}-\ddot{\text{O}}:-$, $:\ddot{\text{N}}=\ddot{\text{O}}:$ and $-\ddot{\text{N}}=\ddot{\text{O}}:+$. Chemically, this oxide shows unsaturated character in the formation of the nitrosyl halides (*e.g.* NOCl), which are believed to be covalent. Alternatively the odd electron may be lost with formation of the nitrosyl or 'nitrosonium' cation $(\text{NO})^+$. Various nitrosyl salts are known, *e.g.* NOClO_4 and NOBF_4 (which are isomorphous with NH_4ClO_4 and NH_4BF_4) and NOHSO_4 (lead chamber crystals).¹⁵ In the co-ordination of nitrosyl groups in complexes (*e.g.* in nitrosyl carbonyls), three electrons are, in effect, donated to the central metal atom (*see p.* 436).

Nitrogen sesquioxide, N_2O_3 , probably exists only in the solid state. The product obtained by condensing and solidifying an equimolecular mixture of NO and NO_2 melts sharply at -103° , the

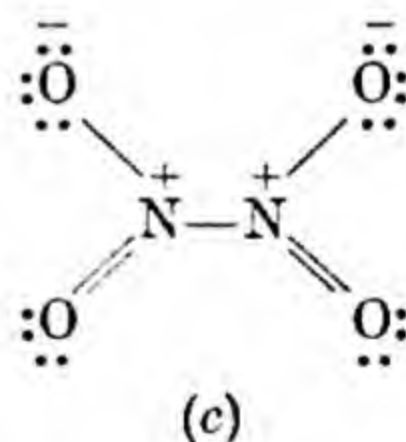
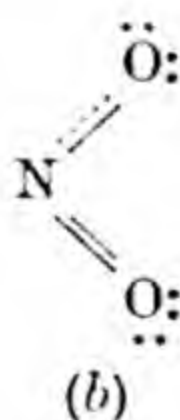
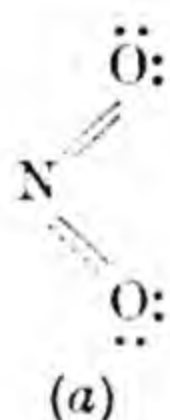
¹⁴ Schomaker and Spurr, *J. Amer. Chem. Soc.*, 1942, **64**, 1184.

¹⁵ Klinkenberg, *Rec. Trav. Chim. Pays Bas*, 1937, **56**, 749.

colour of the melt changing from blue to green with increasing temperature due, it is believed, to increasing dissociation into NO and NO₂. In the vapour phase the molecule is almost completely dissociated.¹⁶ The structure of N₂O₃ has not been established by physical methods. Chemically it behaves as an acid anhydride, giving the unstable nitrous acid with water and nitrites with alkalis. The most probable structure is O=N—O—N=O. On mixing NO₂ enriched in the isotope N¹⁵ with NO containing the nitrogen isotopes in the normal ratio there is a rapid exchange, which is accounted for by the alternative modes of dissociation in the symmetrical structure shown below.¹⁷



Nitrogen Dioxide.—This oxide is so familiar that it is surprising to find that the structure is not yet known with certainty. The monomer, NO₂, an 'odd' molecule, is paramagnetic. Loss of an electron yields the nitronium ion, NO₂⁺, which occurs in concentrated nitric acid, in several well-defined crystalline salts (*e.g.* NO₂ClO₄, NO₂PF₆, (NO₂)₂SnF₆, NO₂AuF₄)¹⁸ and also in solid nitrogen pentoxide (NO₂⁺NO₃[−] : *vide infra*). The NO₂ molecule is non-linear. Thus spectroscopic measurements give the O—N—O bond angle as 110–120°,¹⁹ whereas electron diffraction gives a value of 132 ± 2°, with an N—O distance of 1.20 Å.²⁰ (the theoretical value for N—O is 1.36 and that for N=O 1.15 Å.). Pauling has expressed the structure in terms of resonance between the forms (a) and (b) below :



The structure (c) for the dimer, N₂O₄, is indicated by X-ray measurements on the solid and by spectroscopic measurements,²¹ although a structure with two oxygen atoms bridging the nitrogen

¹⁶ Purcell and Cheesman, *J.C.S.*, 1932, 826.

¹⁷ Liefer, *J. Chem. Physics*, 1940, 8, 301.

¹⁸ Woolf and Emeléus, *J.C.S.*, 1950, 1050.

¹⁹ Sutherland and Penney, *Nature*, 1935, 136, 146.

²⁰ Maxwell and Mosley, *J. Chem. Physics*, 1940, 8, 738. Claesson, Donohue and Schomaker, *ibid.*, 1948, 16, 207.

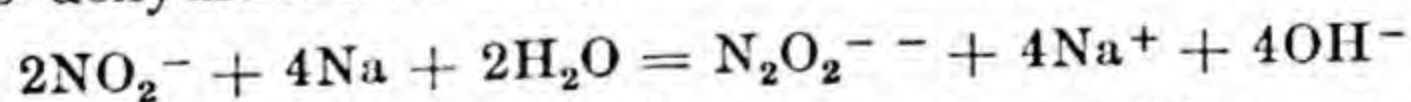
²¹ Hendricks, *Z. Physik*, 1931, 70, 699; Sutherland, *Proc. Roy. Soc.*, 1933, 141, 342.

atoms is not excluded. Chemically, nitrogen dioxide behaves as the mixed anhydride of nitrous and nitric acids.

Nitrogen pentoxide, which is prepared as a white crystalline solid by distilling nitric acid with phosphorus pentoxide, behaves chemically as the anhydride of nitric acid. In the solid state its lattice has been shown to contain the ions NO_2^+ and NO_3^- with N—O distances of 1.15 and 1.24 Å. in the cation and anion respectively.²² Its structure in the vapour state is believed to be $\text{O}_2\text{N—O—NO}_2$, but there is uncertainty as to the N—O—N bond angle. The solid oxide sublimes readily without melting and the vapour phase dissociation into NO_2 and O_2 is familiar as one of the classical examples of a unimolecular reaction.

Nitrogen trioxide was described by Schwarz and Achenbach²³ as a white solid which decomposed above -140° into NO_2 and O_2 . It was prepared by passing NO_2 and O_2 in a ratio 1 : 20 and at a pressure of 1 mm. through a glow discharge in a U-shaped discharge tube, the lower part of which was cooled in liquid air. This work has, however, been criticized by Klemenc and Neumann²⁴ and there is some doubt as to whether the solid compound is formed under such conditions. Several workers have noticed new bands in the absorption spectrum of ozone mixed with either NO_2 or N_2O_5 . Lowry and his co-workers,²⁵ for example, found that when nitrogen pentoxide vapour was mixed with a small proportion of ozone a blue gas was produced which decomposed with luminescence at 100° . It seems probable that under such conditions NO_3 is formed in the gas phase, but that it is very unstable. The solution of the gas in water has strong oxidizing properties, which are not due to hydrogen peroxide. It may be concluded that NO_3 does not contain the peroxide link and that this oxide is not the anhydride of pernitric acid.

Hyponitrous Acid.—Several methods are available for preparing salts of this acid. Sodium nitrite may, for example, be reduced with sodium amalgam, yielding the pentahydrate $\text{Na}_2\text{N}_2\text{O}_2 \cdot 5\text{H}_2\text{O}$, which may be dehydrated in vacuum. The main reaction is:



The free acid is formed as a white crystalline solid on evaporating

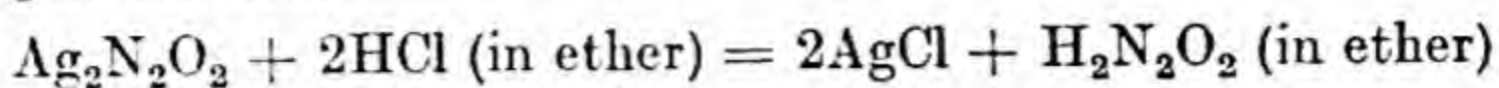
²² Grison, Eriks and de Vries, *Acta Cryst.*, 1950, 3, 290.

²³ *Ber.*, 1935, 68, 343.

²⁴ *Z. anorg. Chem.*, 1937, 232, 216.

²⁵ Lemon and Lowry, *J.C.S.*, 1936, 1409. Lowry and Seddon, *ibid.*, 1937, 1461; 1938, 626. See also Warburg and Leithäuser, *Ann. Phys.*, 1906, 20, 743; 1907, 23, 209. Schumacher and Sprenger, *Z. physikal Chem.*, 1928, 136, 77; 1929, 140, 281; 1929, B, 2, 267. Sprenger, *Z. Elektrochem.*, 1931, 37, 674.

the solution obtained after decomposing the silver salt with ethereal hydrogen chloride



The solid decomposes on standing, or when heated, giving nitrogen, oxides of nitrogen and water. It is soluble in water, but nitrous acid is formed in the solution. The salts are more stable: they and the free acid have strong reducing properties.

Hyponitrous acid is a weak dibasic acid, the values for the first and second ionization constants at 25° being: $k' = 9 \times 10^{-8}$; $k'' = 1.0 \times 10^{-11}$.²⁶ Both acid and normal salts have been prepared. Esters (*e.g.* $(\text{C}_2\text{H}_5)_2\text{N}_2\text{O}_2$) have molecular weights corresponding to the double formula. The molecule may be written as $\text{H}-\text{O}-\text{N}=\text{N}-\text{O}-\text{H}$, but it is probable that it is non-linear and that the (OH) groups occupy the *trans* position, since the esters have a very small moment in solution.²⁷

The dibasic *nitrohydroxylamic acid*, $\text{H}_2\text{N}_2\text{O}_3$, is known only in the form of its salts. The sodium salt was prepared by Angeli²⁸ by the interaction of hydroxylamine hydrochloride, alcoholic sodium ethoxide and ethyl nitrate. Salts of other metals are also known: all are readily oxidized and on acidification evolved nitric oxide. The theoretical anhydride would be N_2O_2 , but the acid is not directly related to any oxide of nitrogen, and its structure is unknown.

Nitrous acid exists only in solution, and even then changes readily to nitric acid and nitric oxide. There is little direct evidence as to the structural formula, but the chemical evidence, especially the formation of nitro ($\text{A}-\text{NO}_2$) and nitrito ($\text{A}-\text{O}-\text{N}=\text{O}$) derivatives, suggests that there is a tautomeric equilibrium between the two forms $\text{A} \rightleftharpoons \text{B}$. The nitrite ion is triangular in shape.

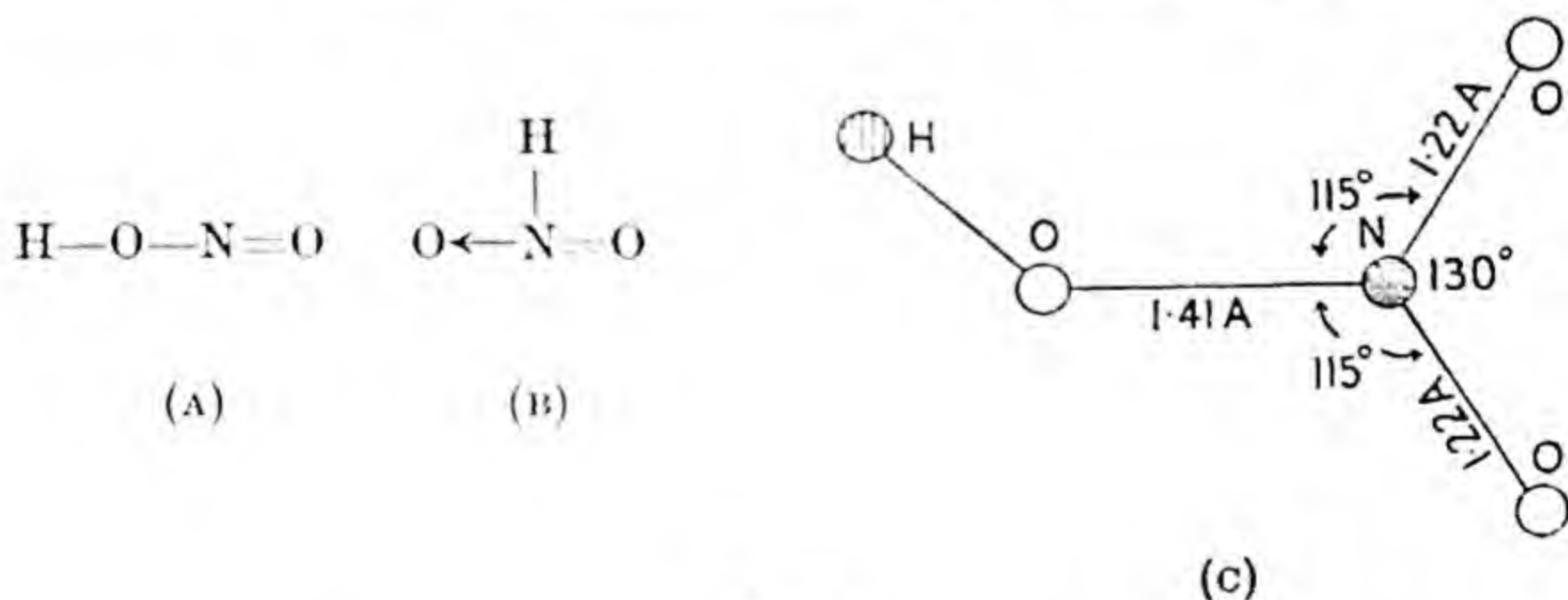


FIG. 52.

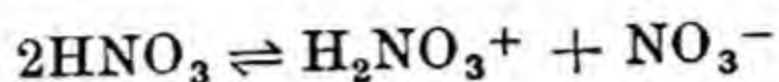
²⁶ Latimer and Zimmerman, *J. Amer. Chem. Soc.*, 1939, 61, 1550.

²⁷ Hunter and Partington, *J.C.S.*, 1933, 309.

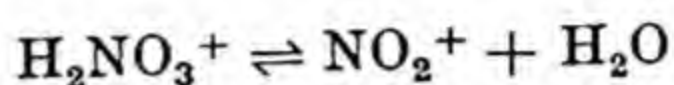
²⁸ *Gazzetta*, 1896, 26, ii, 17.

Nitric acid in the vapour state has been shown by electron diffraction measurements²⁹ to have a planar structure with the dimensions shown on p. 326 (C). The nitrate ion is also planar, like the borate and carbonate ions, and unlike the sulphite and chlorate ions, which are pyramidal.

Pure nitric acid ionizes according to the equation:



(cf. p. 518) but the ion H_2NO_3^+ has a tendency to dissociate as follows:



There is good evidence that the nitrating properties of mixtures of nitric and sulphuric acid are due to the presence of the nitronium cation (NO_2^+).³⁰

Oxides and Oxyacids of Phosphorus.³¹

The formulæ of the oxides of phosphorus, together with the chief oxyacids (excluding the per-acids H_3PO_5 and $\text{H}_4\text{P}_2\text{O}_8$, which are described elsewhere) are shown below:

(P_4O) , (P_2O)	H_3PO_3	Hypophosphorous acid
P_4O_6	H_3PO_3	Phosphorous acid
$(\text{PO}_2)_n$	$\text{H}_4\text{P}_2\text{O}_6$	Hypophosphoric acid
	H_3PO_4	Orthophosphoric acid
P_2O_5	HPO_3	Metaphosphoric acid
(P_2O_5)	$\text{H}_4\text{P}_2\text{O}_7$	Pyrophosphoric acid

The existence of the first two oxides (P_4O and P_2O), which were at one time believed to be formed in the slow oxidation of phosphorus in ether solution, is now regarded as very uncertain. The oxides P_4O_6 and P_4O_{10} , formed respectively in the slow and free combustion of phosphorus, are the anhydrides of the two main series of acids. They are both related structurally to the tetrahedral P_4 molecule as shown below. In P_4O_6 one oxygen atom bridges each pair of phosphorus atoms, while in P_4O_{10} there is an additional oxygen atom joined to each phosphorus atom.³² These results were obtained by an electron diffraction study of the vapours. Sulphur reacts with P_4O_6 forming $\text{P}_4\text{O}_6\text{S}_4$, which is structurally similar to P_4O_{10} , the four additional oxygen atoms being replaced by sulphur.

²⁹ Maxwell and Mosley, *J. Chem. Physics*, 1940, 8, 738.

³⁰ Goddard, Hughes and Ingold, *Nature*, 1946, 158, 480.

³¹ For a discussion of the polyphosphoric acids see p. 227.

³² Hampson and Stosick, *J. Amer. Chem. Soc.*, 1938, 60, 1814.

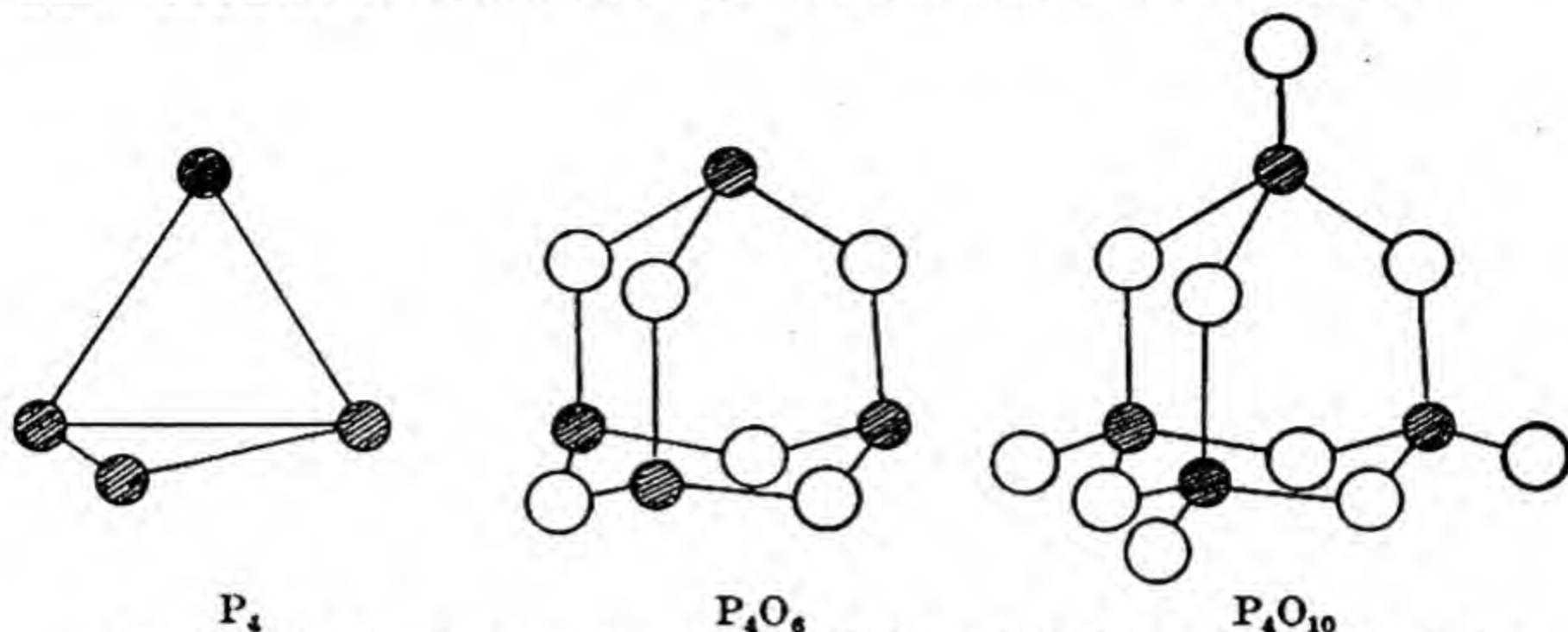
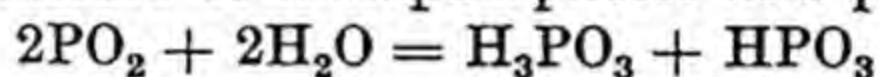


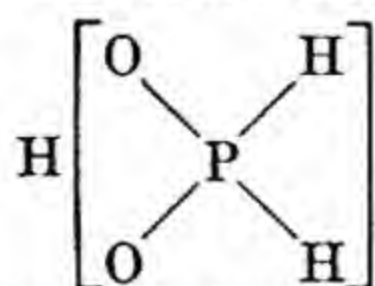
FIG. 53.—Molecular structure of P_4 , P_4O_6 and P_4O_{10} as determined by electron diffraction.

The oxide $(PO_2)_n$ is formed as a well-defined highly crystalline compound (apparently cubic) when P_4O_6 is heated in a sealed tube at $200\text{--}250^\circ$. The vapour density is uncertain and nothing is known of the structure. It reacts with water, evolving some phosphine, and forming a mixture of metaphosphoric and phosphorous acids.

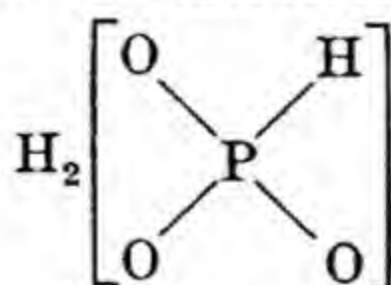


Phosphorus trioxide, PO_3 , is formed when a mixture of phosphorus pentoxide and oxygen at a pressure of about 1 mm. is passed through a discharge tube cooled in ice.³³ A bluish-violet product separates on the cooled tube. This is found to be a mixture of phosphorus pentoxide and the oxide PO_3 . The aqueous solution has strong oxidizing properties and it has been suggested, though not yet proved, that the oxide has the structure $O_2P\text{---}O\text{---}O\text{---}PO_2$ and is the anhydride of perldiphosphoric acid.

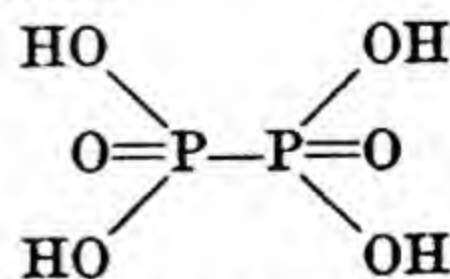
The chemistry of the oxyacids of phosphorus is largely familiar, but their structures present several points of great interest. Hypophosphorous acid, H_3PO_2 , salts of which are formed together with phosphine when phosphorus is heated with an aqueous alkali, may be isolated as a crystalline solid (m.p. 26.5°). The acid has strong reducing properties and is *monobasic*. Furthermore the anion in the hypophosphites of magnesium and nickel has been shown to have a tetrahedral structure, and when the salt KH_2PO_2 is dissolved in deuterium oxide no exchange with the hydrogen atoms occurs. The structure shown below is therefore indicated.



Hypophosphorous acid



Phosphorous acid



Hypophosphoric acid

³³ Schenk and Platz, *Naturwiss.*, 1936, 24, 651; Schenk and Rehaag, *Z. anorg. Chem.*, 1937, 233, 403.

Phosphorous acid, H_3PO_3 , is a dibasic acid, formed in the hydrolysis of phosphorus trichloride, and may also be isolated as crystalline solid. The structure of the phosphite ion in salts has not yet been verified by X-ray studies, but, from the basicity, that shown above is most probable.

Hypophosphoric acid, $\text{H}_4\text{P}_2\text{O}_6$, the sodium salt of which is very conveniently prepared by the controlled reaction of a sodium hypochlorite solution with red phosphorus, may be made by decomposition of the lead salt with hydrogen sulphide. It crystallizes from aqueous solution with two molecules of water, which are lost in vacuum over phosphorus pentoxide. The double formula follows from the fact that the salts are diamagnetic, whereas H_2PO_3 would be an 'odd electron molecule' giving rise to paramagnetic salts. The acid is tetrabasic and the molecular weight of the ethyl ester also corresponds with the formula $(\text{C}_2\text{H}_5)_4\text{P}_2\text{O}_6$. The structure is not yet known with certainty, but is probably best represented by the formula shown above. The formation of the sodium salt by the reaction of alkaline hydrogen peroxide with P_2I_4 suggests that the phosphorus atoms are directly linked, and the relatively feeble reducing properties of hypophosphates are not consistent with the presence of P—H bonds in the molecule.

Oxides and Oxyacids of Sulphur.

The oxides of sulphur known at the present time are tabulated below, while opposite to each is given the formula of the acid of which, in theory at least, it is to be regarded as the anhydride.

	SO	H_2SO_2	Sulphoxylic acid
		$\text{H}_2\text{S}_2\text{O}_3$	Thiosulphuric acid
	S_2O_3	$\text{H}_2\text{S}_2\text{O}_4$	Hydrosulphurous acid
	SO_2	H_2SO_3	Sulphurous acid
	SO_3	H_2SO_4	Sulphuric acid
	S_2O_7	$\text{H}_2\text{S}_2\text{O}_8$	Perdisulphuric acid
	SO_4	H_2SO_5	Permonosulphuric acid

Some of these acids (H_2SO_2 , $\text{H}_2\text{S}_2\text{O}_3$, $\text{H}_2\text{S}_2\text{O}_4$, H_2SO_3) are unknown in the free state, although all have been characterized by definitely established salts or other derivatives. The oxides SO and SO_4 have been discovered recently and merit special attention. The remainder have been known for many years and only in the case of the heptoxide, S_2O_7 , is there any doubt as to the identity.

Sulphur Monoxide.—This oxide was first prepared in 1933 by Cordes and Schenk³⁴ by passing an electric discharge through a streaming mixture of sulphur vapour and sulphur dioxide at a pressure between a few millimetres and a few centimetres of mercury.

³⁴ *Z. anorg. Chem.*, 1933, 211, 150.

On passing the issuing gas through a U-tube cooled in liquid air an orange-red deposit was formed: when allowed to melt it decomposed slowly into sulphur and sulphur dioxide in a 1:1 ratio. Sulphur monoxide is also produced when an electrical discharge is passed through sulphur dioxide, in the regulated combustion of sulphur in oxygen, in the thermal decomposition of thionyl bromide (520°) or thionyl chloride (900°), or when thionyl chloride reacts with stannous chloride or with metals such as tin, sodium or antimony. Some of these methods give very low yields.

In all of these reactions the monoxide is readily detected by means of a characteristic ultra-violet absorption spectrum at 2488–3396 Å. The bands are observed by photographing the absorption spectrum of the gaseous material formed in one of the above preparative methods. Their intensity gives a measure of the amount of oxide present, and in this way the oxide has been shown to be stable at room temperature in dry glass for several days, but to be decomposed rapidly at 100° . It has been suggested that the absorption bands are due to a metastable S_2 molecule,³⁵ but as Schenk³⁶ points out they are never observed in the absence of oxygen. There is, however, an element of doubt as to the true molecular species responsible, and it is important that this be removed.

The monoxide reacts readily with metals, forming sulphides, and with chlorine and bromine to yield the corresponding thionyl halides. On sparking with oxygen sulphur dioxide is formed, and the reaction with water at 0° gives sulphur, hydrogen sulphide and sulphur dioxide. There is some evidence that the orange-red solid which separates in the discharge tube during the preparation of the monoxide is a mixture of polymeric materials, and not the solid monoxide. The evidence as to the nature of these compounds is neither definite nor convincing, but it is possible that polysulphur oxides containing a short chain of sulphur atoms are formed, and that sulphur monoxide is a degradation product of these.

Sulphur Sesquioxide.—The blue-green oxide S_2O_3 is formed by adding dry sulphur to liquid sulphur trioxide. Excess of the latter may be poured off (it does not dissolve S_2O_3), and the last traces removed in a stream of carbon dioxide. The oxide decomposes slowly at room temperature, forming sulphur and the di- and tri-oxides. It reacts with water to give free sulphur together with sulphuric, sulphurous, and tri-, tetra- and pentathionic acids.

³⁵ Cordes, *Z. Physik*, 1937, **105**, 251.

³⁶ *Ibid.*, 1937, **106**, 271.

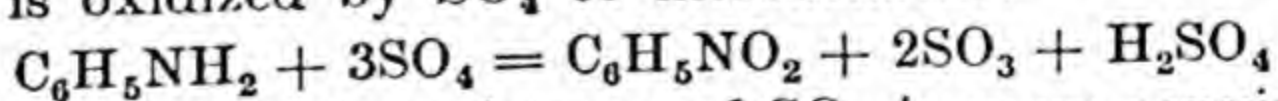
³⁷ Schenk, *Z. anorg. Chem.*, 1941, **248**, 297; *Z. physikal. Chem.*, 1942, **B**, **51**, 113.

From the formula, the sesquioxide should be the anhydride of hydrosulphurous acid, but neither this acid nor its salts can be obtained from S_2O_3 . The vapour density cannot be determined because of the ready decomposition, and no solvent has been found in which the oxide dissolves without reaction. At present, therefore, the structure must be regarded as completely unknown.

Sulphur Heptoxide and Sulphur Tetroxide.—The compound S_2O_7 was first prepared in 1878 by Berthelot by passing a mixture of sulphur dioxide with an excess of oxygen through a silent electric discharge. Oily drops are formed, which crystallize at about 0° , though Meyer, Bailleul and Henkel³⁸ found that the crystalline product described by Berthelot was formed only when excess of sulphur trioxide was employed. Maisin,³⁹ in attempting to repeat this work, obtained a product to which the formula S_3O_{11} was assigned.

Sulphur tetroxide, SO_4 , was prepared by Schwarz and Achenbach⁴⁰ by a very similar method. Sulphur dioxide and oxygen in a ratio of 1 : 10 were passed at a total pressure of 0.5 mm. through a glow discharge and the product was frozen out in liquid air. The white material which separated was readily freed from dioxide and ozonized oxygen by allowing it to warm to -30° in a stream of oxygen. The residue was a white solid, some 0.1 gram of which was obtained by operating the discharge tube for 6 hours. The white material was analysed by adding potassium iodide solution through a dropping funnel, and estimating the iodine formed volumetrically and the sulphate gravimetrically. A ratio of SO_3 to active oxygen of 1 : 1 was obtained, while the molecular weight as determined from the depression of the freezing-point of sulphuric acid was found to correspond with the formula SO_4 .

Sulphur tetroxide melts at 3° and above this temperature loses oxygen and forms S_2O_7 . With aqueous alkali it gives a salt of perdisulphuric acid,⁴¹ but there is no evidence that either $H_2S_2O_8$ or H_2SO_5 is formed with water. Sulphur heptoxide, on the other hand, is said to give some perdisulphuric acid with water. Both SO_4 and S_2O_7 have very strong oxidizing properties. Aniline, for example, is oxidized by SO_4 to nitrobenzene.



The evidence for the existence of SO_4 is more convincing than that for S_2O_7 , though it is by no means complete. It is possible that S_2O_7 is a mixture containing SO_4 and SO_3 , but this point cannot yet be decided.

³⁸ *Ber.*, 1922, 55, 2923.

³⁹ *Bull. Soc. Chim. Belg.*, 1928, 37, 326.

⁴⁰ *Z. anorg. Chem.*, 1934, 219, 271.

⁴¹ Fichter and Maritz, *Helv. Chim. Acta*, 1939, 22, 792.

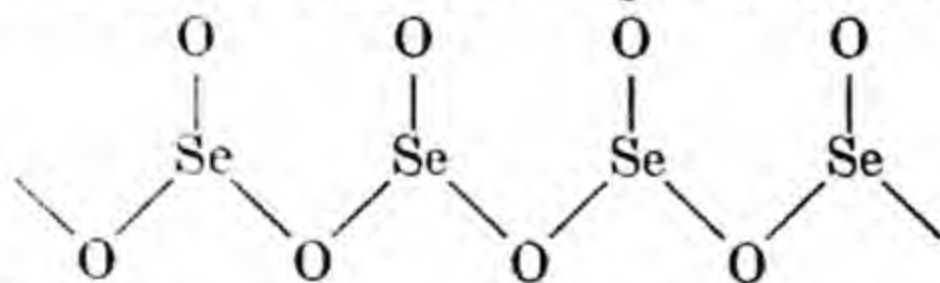
Mixed Oxides of Selenium, Tellurium and Sulphur.

When selenium is dissolved in liquid sulphur trioxide a green solid separates from which most of the excess sulphur trioxide may be poured off, the last traces being removed by evaporation in vacuum. The green substance has the formula SeSO_3 . It decomposes into selenium and sulphur trioxide when gently heated, but is said to be rather more stable than S_2O_3 . The tellurium compound, TeSO_3 , is made similarly but is considerably more stable. When heated in vacuum at 180° it decomposes into tellurium monoxide and sulphur dioxide. According to Schenk ⁴² there is no indication of the formation of selenium monoxide either by the thermal decomposition of SeSO_3 or by other methods, such as the passage of a mixture of the vapours of selenium and selenium dioxide through an electrical discharge.

Selenium Oxides.

Selenium gives two oxides, SeO_2 and SeO_3 . The first is formed by oxidizing selenium in air or oxygen, or by heating it with nitric acid. It forms fine white needle-shaped crystals which yield the acid H_2SeO_3 with water. This acid is much more stable than sulphurous acid and may be isolated as a crystalline solid by evaporation of its aqueous solution in vacuum over sulphuric acid. The crystals readily lose water and revert to the dioxide. The acid is oxidized to selenic acid only by powerful oxidizing agents such as potassium permanganate, and differs in this respect from sulphurous acid, which is readily oxidized.

Selenium dioxide has an interesting lattice which contains long chains of the type shown below, bound together by weaker lateral forces. Sulphur dioxide exists as single molecules



and tellurium dioxide, which is dimorphous, forms ionic crystals.

Selenium trioxide has defied attempts to prepare it by the more obvious methods, but is produced admixed with selenium dioxide by the action of a high-frequency discharge on a mixture of selenium and oxygen at a pressure of 15–20 mm.⁴³ The product contains 20–36 per cent of the trioxide and gives the corresponding mixture of selenite and selenate ions when treated with water. The fact that no monoxide of selenium is known has been mentioned already.

⁴² *Z. anorg. Chem.*, 1937, 233, 401.

⁴³ Rheinboldt, Hessel and Schwenzer, *Ber.*, 1930, 63, 84, 1865.

Tellurium Oxides.

Tellurium forms the oxides TeO , TeO_2 , and TeO_3 . The first of these, TeO , is obtained by decomposing the oxide TeSO_3 , which is formed from sulphur trioxide and tellurium, at 180° in vacuum. In spite of Damiens' assertion⁴⁴ that it has all the properties of a mixture of tellurium and tellurium dioxide, the analytical data correspond to the formula TeO and the compound (a black powder) decolorizes potassium permanganate instantly in the cold.⁴⁵ On heating in vacuum it is converted to Te and TeO_2 . No lower acid of tellurium derived from this oxide has so far been obtained.

Tellurium dioxide, TeO_2 , is formed by burning tellurium in air or oxygen, oxidizing tellurium with nitric acid, decomposing tellurites with acids, or by heating basic salts of tellurium (*vide infra*). It is a crystalline solid which, unlike the sulphur and selenium analogues, has a low solubility in cold water (1 in 150,000). It is readily reduced to tellurium. The oxide is amphoteric. Thus, for example, it dissolves in hydrochloric acid, forming the tetrachloride. Nitric acid under certain conditions forms the basic nitrate 2TeO_2 , HNO_3 , and sulphuric acid the basic sulphate 2TeO_2 , SO_3 , both of which are decomposed by water to give the dioxide.

Tellurous acid, a very weak acid, is unstable and rapidly loses water when liberated from tellurites by the addition of stronger acids, tellurium dioxide being precipitated. The tellurites, on the other hand, are relatively stable salts. Some are derived from H_2TeO_3 , but salts of condensed acids such as $\text{H}_2\text{Te}_2\text{O}_5$ and $\text{H}_2\text{Te}_4\text{O}_9$ are also known.

Telluric acid differs markedly from sulphuric and selenic acids. When tellurium is dissolved in aqua regia with the addition of chloric acid the compound H_6TeO_6 may be obtained from solution and re-crystallized from water. This is the ortho form and the most stable. It is a weak hexabasic acid, and both normal and acid salts are known. The six OH groups have been shown by X-ray analysis to be arranged octahedrally round the tellurium atom. The acid dissolves sparingly in cold but readily in hot water. When the ortho acid is heated in a sealed tube to 140° it is converted to a polymerized acid $(\text{H}_2\text{TeO}_4)_n$, known as allotelluric acid, a syrup which is miscible with water, and which, with excess water, reverts to the ortho form. Allotelluric acid is stronger than the ortho acid. Both acids are readily reduced to tellurium. Tellurates derived from H_2TeO_4 , or more complex condensed acids, are formed by fusing tellurites with potassium nitrate or when chlorine is passed

⁴⁴ *Compt. rend.*, 1924, 179, 829.

⁴⁵ Doolan and Partington, *J.C.S.*, 1924, 125, 1402.

into an alkaline solution of a tellurite. With a few exceptions (*e.g.* K_2SO_4 , K_2SeO_4 , K_2TeO_4) tellurates are not isomorphous with sulphates and selenates. When they are treated with a strong acid orthotelluric acid is formed.

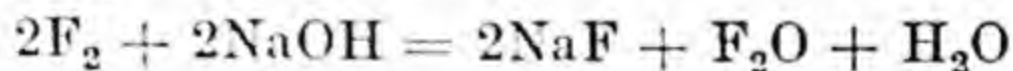
Tellurium trioxide is formed when H_6TeO_6 is heated to 360° . At higher temperatures tellurium dioxide and oxygen are produced. The oxide is insoluble in cold water but, with boiling water, slowly forms the ortho acid. It functions as an oxidizing agent, dissolving in hot concentrated hydrochloric acid with liberation of chlorine. With hot concentrated alkali it forms tellurates.

Oxides and Oxyacids of the Halogens.

The table below shows the formulæ of the well-established oxides and oxyacids of the halogens. As is pointed out in detail later, a number of the oxyacids cannot be isolated in the pure state, though their salts have been fully characterized. The oxides of fluorine and bromine are relatively new. There is as yet no convincing evidence for the existence of oxyacids of fluorine or their salts.

F_2O , F_2O_2	
Cl_2O , ClO_2 , $\text{ClO}_3(\text{Cl}_2\text{O}_6)$	HClO , HClO_2 , HClO_3
Cl_2O_7 , (ClO_4)	HClO_4
Br_2O , BrO_2 , Br_3O_8	HBrO , HBrO_2 , HBrO_3
IO_2 , I_4O_9 , I_2O_5	HIO_4 , $\text{H}_4\text{I}_2\text{O}_9$, H_5IO_6

Oxides of Fluorine.—The discovery that fluorine forms an oxide was made in 1927 by Lebeau and Damiens,⁴⁶ who found that in the presence of water the electrolysis of molten acid potassium fluoride at below 100° yielded an oxygen compound of fluorine to which the formula F_2O was given. Two years later⁴⁷ the same authors described the preparation of fluorine monoxide in a 70 per cent yield by bubbling fluorine at the rate of 1 litre per hour through a platinum tube dipping just below the surface of a 2 per cent aqueous sodium hydroxide solution. The reaction taking place is



The conditions for the preparation are critical. The boiling-point of F_2O is -144.8° .⁴⁸ It is slightly endothermic, but differs from Cl_2O in being non-explosive. Fluorine monoxide is, nevertheless, very reactive and is decomposed by nearly all metals on heating, forming fluorides and oxides. Phosphorus is converted to phosphorus oxyfluoride and sulphur to a mixture of sulphur dioxide and tetrafluoride. When mixed with hydrogen and sparked it explodes, and will also explode with chlorine, although the reaction,

⁴⁶ *Compt. rend.*, 1927, 185, 652.

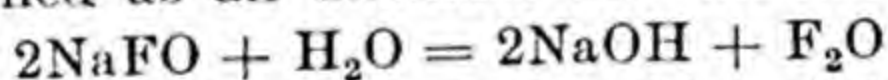
⁴⁷ *Ibid.*, 1929, 188, 1253.

⁴⁸ Ruff and Menzel, *Z. anorg. Chem.*, 1931, 198, 39.

in which chlorine monofluoride is formed, never goes to completion. Fluorine monoxide is moderately soluble in water (6.8 c.c. per 100 c.c. at 0°) and Henry's law is obeyed. The solution has strong oxidizing properties, but is not acidic, nor does it yield hypofluorites when treated with alkalis. The compound CF_3OF , which may be regarded as a fluoroalkyl hypofluorite, is, however, formed in the fluorination of methyl alcohol or carbon monoxide with silver fluoride and fluorine.⁴⁹ It is a gas (b.p. -95°) which has strong oxidizing properties and is thermally stable up to 450° .

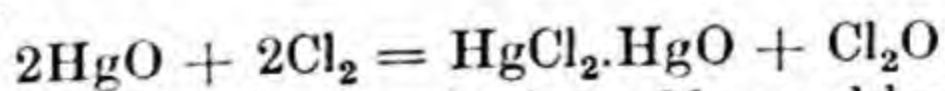
The second oxide of fluorine, F_2O_2 , is formed when a mixture of fluorine and oxygen is passed through a silica U-tube into which two electrodes are sealed.⁵⁰ A discharge is passed through the streaming gas with the tube cooled in liquid air, when a yellow solid separates on the cooled surface. This is stable only below -100° , above which temperature it decomposes into fluorine and oxygen. The molecular formula, F_2O_2 , has been established by vapour density measurements below -100° . Nothing is known of the reactions of this oxide. Its structure is likewise unknown.

Oxyacids of Fluorine.—Hypofluorous acid and fluoric acid have not yet been prepared. It is possible that in the preparation of fluorine monoxide, the gas is formed by the hydrolysis of sodium hypofluorite, formed as an unstable intermediate



When a 50 per cent potassium hydroxide solution is fluorinated at -50° and the product evaporated and repeatedly fused, the product retains some oxidizing properties, which might be due to the presence of a fluorate.⁵¹ Again, it has been claimed that when a molten mixture of potassium hydroxide and fluoride is electrolysed in a silver crucible, which served as cathode, with a graphite anode, the product, when dissolved in water and acidified with nitric acid, gives a precipitate containing silver and fluoride. This may have contained silver fluorate, since silver fluoride is soluble. These experiments have not, however, been carried further and are at present unconvincing.

Oxides of Chlorine.—Chlorine monoxide (b.p. 2°) is normally prepared by passing chlorine over dry mercuric oxide, previously heated to 300° .



It reacts with water forming a solution of hypochlorous acid, but the free acid is known only as the hydrate $\text{HClO} \cdot 2\text{H}_2\text{O}$ (m.p. -36°).⁵²

⁴⁹ Kellogg and Cady, *J. Amer. Chem. Soc.*, 1948, 70, 3986.

⁵⁰ Ruff and Menzel, *Z. anorg. Chem.*, 1933, 211, 204.

⁵¹ Dennis and Rochow, *J. Amer. Chem. Soc.*, 1933, 55, 2431.

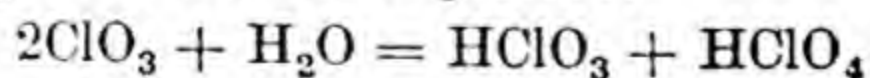
⁵² Secoy and Cady, *ibid.*, 1940, 63, 1036.

This oxide is familiar as a strong oxidizing agent and because of its highly explosive character.

Chlorine dioxide (b.p. 11°) is formed as one of the products of the decomposition of chlorates by concentrated sulphuric acid. The compound is endothermic and the gaseous product of this reaction explodes very readily. Liquid chlorine dioxide is also a dangerously explosive material. A more stable mixture with carbon dioxide is formed when potassium chlorate is reduced by heating with oxalic acid and water. Chlorine dioxide is freely soluble in water and the hydrate $\text{ClO}_2 \cdot 8\text{H}_2\text{O}$ may be isolated. If exposure to light is avoided the gas may be recovered unchanged from water solution. In the light, however, HCl and HClO_4 are formed, while with alkalis a chlorate and a chlorite result. With dilute fluorine, ClO_2 reacts to form ClO_2F (b.p. -6°), which is more stable than chlorine dioxide.⁵³

Chlorine dioxide is a molecule with an odd number of electrons and is paramagnetic. Electron diffraction measurements have shown it to be triangular, with an $\text{O}-\text{Cl}-\text{O}$ valency angle of about 135° (which is somewhat larger than the $\text{Cl}-\text{O}-\text{Cl}$ angle in Cl_2O). The $\text{Cl}-\text{O}$ distance is 1.53, as opposed to 1.68 Å. in Cl_2O , which suggests some measure of double bond character in the two equivalent $\text{Cl}-\text{O}$ bonds of ClO_2 .

The oxide Cl_2O_8 is best made by mixing ozonized oxygen with a second stream of oxygen carrying chlorine dioxide, freezing out the product and fractionating it.⁵⁴ The oxide is a liquid with an extrapolated boiling-point of 203° . The molecular weight in carbon tetrachloride has been determined cryoscopically and is only about ten per cent less than the value corresponding to the molecular form Cl_2O_8 . The liquid is also diamagnetic, whereas ClO_3 would be paramagnetic. The magnetic data are, however, consistent with the presence of a small proportion of ClO_3 . The vapour is probably largely associated to ClO_3 , but decomposes very readily to chlorine and oxygen. When the vapour is mixed with water vapour and cooled, chloric and perchloric acid are the main products. The reaction with liquid water is explosive.



Chlorine heptoxide, the anhydride of perchloric acid, may be obtained by dehydrating pure perchloric acid with phosphorus pentoxide at or below -10° and distilling in vacuum. It is a colourless oil, with an extrapolated boiling-point of 80° . With water it regenerates perchloric acid slowly. It explodes on shock,

⁵³ Schmitz and Schumacher, *Z. anorg. Chem.*, 1942, 249, 238.

⁵⁴ Goodeve and Richardson, *J.C.S.*, 1937, 294.

but is more stable than the other chlorine oxides. The Raman spectrum shows that the molecule has two ClO_2 groups joined by an oxygen bridge, with a Cl—O—Cl angle of 128° .⁵⁵ The dipole moment in carbon tetrachloride is 0.72 ± 0.02 D., which is also consistent with a non-linear molecule.

The existence of chlorine tetroxide, ClO_4 , is extremely doubtful. Silver perchlorate is soluble in various organic solvents and it is possible that in an inert material such as ether the reaction with iodine is :



Silver iodide is precipitated and the ether solution, besides reacting with water to form perchloric acid, gives perchlorates on treatment with metals such as zinc, magnesium, tin, bismuth and silver.⁵⁶ These reactions can be explained if the above reaction yields IClO_4 .

Oxides of Bromine.—The three oxides of bromine, Br_2O , Br_3O_8 and BrO_2 , have all been prepared comparatively recently. The first, Br_2O , was obtained by the action of bromine vapour on specially prepared and dried mercuric oxide at $50\text{--}60^\circ$.⁵⁷ This method resembles the preparation of chlorine monoxide by the action of chlorine on mercuric oxide, but the yields were low and the pure compound was not isolated. Pure Br_2O was first isolated by Schwarz and Wiele⁵⁸ by the decomposition of BrO_2 at room temperature in vacuum. It was found to decompose with evolution of oxygen even at -16° . The primary reaction with water and alkali gave hypobromous acid or a hypobromite, though in the latter case some bromate was also formed.

Bromine dioxide, BrO_2 , has been made by streaming a mixture of bromine vapour and oxygen at low pressure through a U-shaped discharge tube which was cooled in liquid air at its lower end.⁵⁹ The oxide decomposed at temperatures above -40° , one of the products being Br_2O (*vide supra*). The published descriptions of this compound imply that it, and also Br_2O , were less liable than their chlorine analogues to decompose explosively. In its reaction with aqueous alkali, bromate, bromite, hypobromite and bromide were formed.

The oxide Br_3O_8 is formed as a white crystalline solid in the reaction of excess of ozone with bromine vapour at -5° to 10° .⁶⁰ It is fairly stable at -80° and may be decomposed without explo-

⁵⁵ Fonteyne, *Natuurwet. Tijds.*, 1938, 20, 275.

⁵⁶ Gomberg, *J. Amer. Chem. Soc.*, 1923, 43, 398.

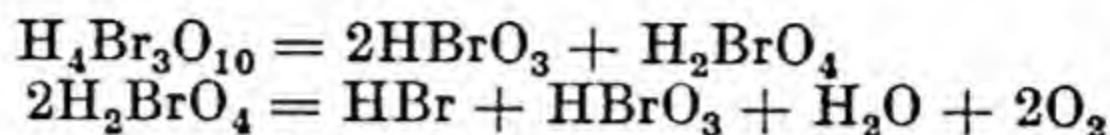
⁵⁷ Zintl and Rienäcker, *Ber.*, 1930, 63, 1098.

⁵⁸ *J. prakt. Chem.*, 1939, (ii), 152, 157.

⁵⁹ Schwarz and Schmeisser, *Ber.*, 1937, 70, 1163.

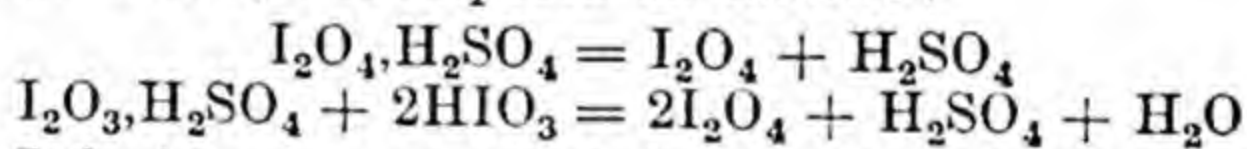
⁶⁰ Lewis and Schumacher, *Z. anorg. Chem.*, 1929, 182, 182.

sion at somewhat higher temperatures into bromine and oxygen. This fact was used in analysing the material. The oxide dissolves readily in water and the oxidizing properties of the solution are accounted for by assuming the primary product to be $\text{H}_4\text{Br}_3\text{O}_{10}$ (for which, however, there is no other evidence), which decomposes as follows:—

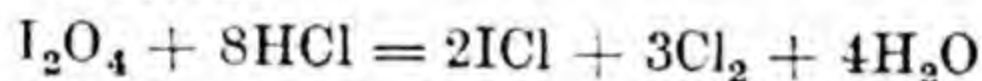


The molecular weight of Br_3O_8 has not been verified by cryoscopic measurements, nor is there any evidence bearing on its structure.

Oxides of Iodine.—There are three oxides of iodine, I_2O_4 , I_4O_9 and I_2O_5 , all of which are solids and which, in their reactions, have little in common with the oxides of the other halogens. The lowest oxide, which is commonly formulated as I_2O_4 , though its molecular weight is unknown, is obtained as a granular yellow powder by the action of hot concentrated sulphuric acid on iodic acid.⁶¹ The first product of this reaction is believed to be a mixture with iodic acid of the two sulphates $\text{I}_2\text{O}_3\cdot\text{H}_2\text{SO}_4$ and $\text{I}_2\text{O}_4\cdot\text{H}_2\text{SO}_4$, which, when treated with water, decomposes as follows:

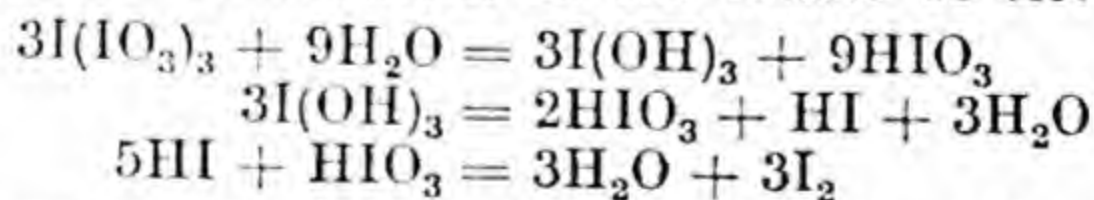


The oxide I_2O_4 is only very slightly soluble in cold water, but dissolves in hot water to form iodic acid and iodine. With hydrochloric acid chlorine is evolved.



The oxide decomposes into iodine pentoxide and iodine when heated to 130° . It has been suggested that I_2O_4 be formulated as a basic iodate of trivalent iodine $(\text{IO})\text{IO}_3$.

The oxide I_4O_9 is formed as a yellow solid in the reaction of ozonized oxygen with iodine which is gently warmed. Reaction occurs in the gas phase. The product is hygroscopic and with water forms a mixture of iodine and iodic acid, a reaction which is consistent with its formulation as the iodate of trivalent iodine.



Thermal decomposition into iodine pentoxide, iodine and oxygen occurs rapidly at 120° .

Iodine pentoxide is produced by refluxing iodine with fuming nitric acid. It yields iodic acid with water. Iodic acid is also dehydrated to the pentoxide at *ca.* 200° . The oxide is a non-volatile white crystalline substance with strong oxidizing properties.

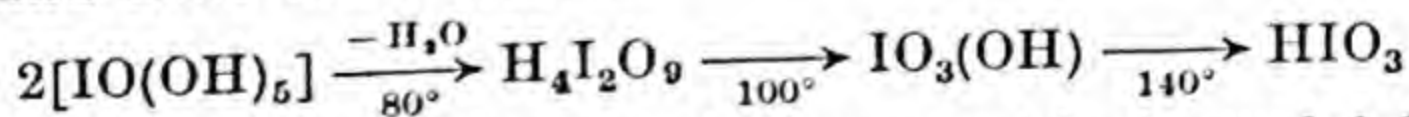
⁶¹ Bahl and Partington, *J.C.S.*, 1935, 1258.

Oxyacids of Chlorine, Bromine and Iodine.

A general comparison of the oxyacids of the halogens shows that for the type HXO , the three acids are known only in aqueous solution. Their strengths and stabilities decrease from $HClO$ to HIO . Hypoiodous acid changes very rapidly in solution to iodic acid and the salts, which cannot be isolated, likewise change to iodates. The hypobromites $NaBrO \cdot 5H_2O$ and $KBrO \cdot 3H_2O$ have recently been prepared by the addition of bromine to solutions of $NaOH$ and KOH cooled below 0° . They were found to decompose even at 0° into bromide and bromate.⁶²

The only oxyacid of the type HXO_2 known with certainty to exist in solution is $HClO_2$. A number of its salts have also been prepared. Acids of the type HXO_3 are known for all three halogens, although $HClO_3$ and $HBrO_3$ cannot be isolated in the pure state. The stability increases from chloric to iodic acid. Salts of these acids are well known and the ions have been shown to be pyramidal, with the halogen atom situated above the plane of the three oxygen atoms.

Perchloric and periodic acids and their salts are also well known, but perbromates (M^+BrO_4) have never been prepared. The periodates are also much more complex than the perchlorates, all of which are derived from $HClO_4$. The commonest form of periodic acid has the formula H_5IO_6 and occurs in Chili saltpeter as sodium periodate. It is a pentabasic acid which forms acid salts. It is obtained by dissolving iodine in caustic soda solution and passing chlorine, when the salt $Na_2H_3IO_6$ separates. This sodium salt is suspended in water and treated with silver nitrate, when the salt Ag_3IO_5 is deposited. The latter is suspended in water and decomposed by chlorine, and, on filtering off the silver chloride and evaporating over concentrated sulphuric acid, deliquescent white crystals of H_5IO_6 are obtained.⁶³ When heated in vacuum at 100° water is lost and the meta acid HIO_4 results, the acid $H_4I_2O_9$ being an intermediate.⁶⁴ When HIO_4 is heated to 140° oxygen is lost and iodic acid formed.



Periodic acid also forms heteropoly anions with the molybdate and tungstate anions.

⁶² FIAT Review of German Science, Inorganic Chemistry, Part I, 172.

⁶³ Vanino, *Präparative Chemie*, Vol. I, 66.

⁶⁴ Partington and Bahl, *J.C.S.*, 1934, 1088.

CHAPTER XI

RECENT CHEMISTRY OF THE NON-METALS ¹

Compounds of the Rare Gases.—The question as to whether the rare gases form compounds or not is still very open. Booth and Willson ² carried out a thermal analysis of the system argon-boron trifluoride, and from the existence of a series of maxima in the freezing-point-composition curve concluded that the following compounds exist in the temperature range -127° to -133° : $A.BF_3$; $A.2BF_3$; $A.3BF_3$; $A.6BF_3$; $A.8BF_3$; $A.16BF_3$. Recently, however, Wiberg and Karbe, ³ in attempting to extend these observations to krypton and xenon, which should form more stable compounds, found that none of the three rare gases was miscible in the liquid state with boron trifluoride. They concluded that no compounds were formed and that the earlier observations were in error. They were also unable to confirm Nikitin's observations ⁴ of compound formation between xenon and sulphur dioxide, hydrogen sulphide, dimethyl ether or methyl alcohol. A compound, $Xe.2C_6H_5OH$, with a dissociation pressure at 0° of 1 atm. has been claimed, ⁵ and the existence of this has not as yet been questioned.

The existence of hydrates of the rare gases appears to be well authenticated, though their compositions are somewhat doubtful. The following melting-points and dissociation pressures are given by de Forcrand : ⁶

	A, xH_2O	$Kr, 5H_2O$	Xe, xH_2O
Melting-point	8°	13°	24°
Dissociation pressure (0°) . .	98 atm.	15.5 atm.	1.3 atm.

¹ In reviewing the recent contributions in this field it is impossible to mention even the major part of the important work which has appeared within, say, the last twenty years. The topics selected appear to the authors to have a special interest in current research, or to be promising fields for further investigation.

² *J. Amer. Chem. Soc.*, 1935, 57, 2273.

³ *Z. anorg. Chem.*, 1948, 256, 307.

⁴ *Z. anorg. Chem.*, 1936, 227, 81. *J. Chem. gén.*, 1939, 9, 1167, 1176. *Compt. rend. Acad. Sci., U.R.S.S.*, 1939, 24, 562, 565.

⁵ Nikitin, *Compt. rend. Acad. Sci., U.R.S.S.*, 1940, 29, 571.

⁶ *Compt. rend.*, 1923, 176, 355; 1925, 181, 15.

The existence of the krypton compound was confirmed by Tammann and Krige,⁷ and the deuterates $\text{Kr}, 6\text{D}_2\text{O}$ and $\text{Xe}, 6\text{D}_2\text{O}$ have also been prepared.⁸ All of these compounds exist only in the solid state and are believed to be van der Waals crystal aggregates like the solid hydrates of methane and methyl bromide.⁹ From time to time the formation of helium compounds of metals such as mercury, tungsten and platinum has been reported. These have usually been obtained by sparking the rare gas in the presence of the metal. Though the metals after this treatment undoubtedly contain considerable amounts of helium, it is probably adsorbed on the dispersed metal, as it is very readily removed and has not been shown to change the lattice dimensions of the metal.

It is convenient at this point to refer to a new group of molecular compounds, the so-called clathrate compounds, several of which

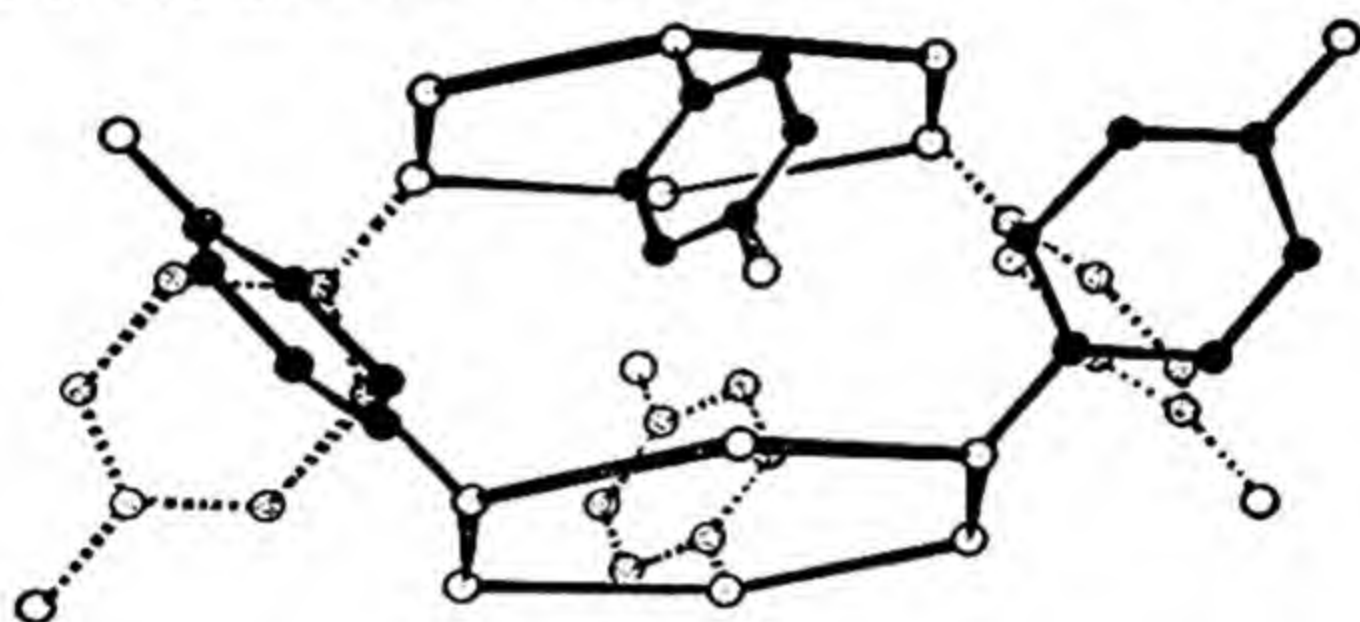


FIG. 54.

contain rare gas atoms.¹⁰ The underlying principle in their formation is the crystallization together of two substances, the molecules of one of which in the solid state form a series of 'cages' into which atoms or molecules of the second compound can fit, but from which they cannot readily escape.

Among the compounds which, in their crystallization, can build up such cages are several aromatic nitro compounds, quinol and urea. In general these compounds, when they crystallize with a second component to form a clathrate compound, do not do so in their normal forms. The dimensions of the cages formed also limit the sizes (and particularly the length) of molecules capable of functioning as the second component. Considering as examples the

⁷ *Z. anorg. Chem.*, 1925, 146, 179.

⁸ Godchot, Cauquil and Calas, *Compt. rend.*, 1936, 202, 759.

⁹ Sidgwick, *The Chemical Elements and their Compounds* (Oxford University Press, 1950), Vol. I, p. 9. For structural determinations see Claussen, *J. Chem. Phys.*, 1951, 19, 259, 662, 1425.

¹⁰ Powell, *J.C.S.*, 1948, 61, 571, 815. Powell and Rayner, *Nature*, 1949, 163, 566.

compounds formed by quinol, among which are some with the rare gases, we find that the second component may be any one of such different molecules as H_2S , SO_2 , HCl , HBr , HCN , CO_2 , C_2H_2 , A , Kr , Xe , all of which are of the right size to fit into the quinol structure. Each enclosed molecule is in a separate cage, the nature of which may be seen from Fig. 54. This shows the positions of the centres of the atoms making up the six quinol molecules which surround each argon atom. When the actual space occupied by the atoms which make up the framework is taken into account the enclosure is much more complete. The quinol molecules are held together by hydrogen bonds.

The compound has approximately the composition $(\text{C}_6\text{H}_6\text{O}_2)_3\text{A}$ and is a stable crystalline solid with a negligible argon pressure. Argon is set free only when the hydrogen bonds in the quinol structure are broken by heating or by the action of a solvent. The argon is prevented from escaping by the smallness of the gaps in the cage, in passing through which it would encounter strong repulsive forces.

Some Compounds of Silicon.

The halides of silicon differ considerably from those of carbon, notably in the much greater ease with which they are hydrolysed. A number have been prepared containing two different halogen atoms in the molecule (*e.g.* SiFCl_3 , SiClBr_3 , SiBrI_3 , SiICl_3). Members of the homologous series $\text{Si}_n\text{Cl}_{2n+2}$ are known up to $n = 4$, although our knowledge of the corresponding derivatives of the other halogens is less extensive and there are indications that the highest fluoride is Si_2F_6 .

Silicon also has a striking tendency to form chlorides of much greater complexity. Thus when silicon tetrachloride vapour mixed with argon is heated to $1000\text{--}1100^\circ$ the compounds $\text{Si}_{10}\text{Cl}_{22}$ and $\text{Si}_{25}\text{Cl}_{52}$ are formed. The molecular weights have been determined in benzene solution.¹¹ If the argon is replaced by hydrogen the compound $\text{Si}_{10}\text{Cl}_{20}\text{H}_2$ results. Both of these chlorides when heated at 300° give a complex mixture of products which include a highly polymerized monochloride $(\text{SiCl})_n$.¹² A monoiodide $(\text{SiI})_n$ is formed similarly by cracking Si_2I_6 .¹³ These monohalides have strong reducing properties. All of the compounds mentioned are readily

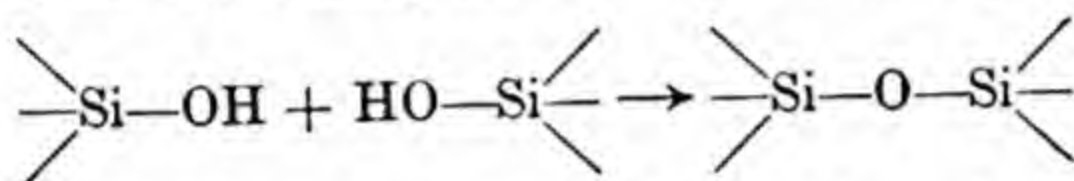
¹¹ Schwarz and Meckbach, *Z. anorg. Chem.*, 1937, 232, 241. FIAT Review of German Science, Inorganic Chemistry, Part I, p. 260.

¹² Schwarz and Thiel, *Z. anorg. Chem.*, 1938, 235, 247. See also Hertwig and Wiberg, *Z. Naturforschg.*, 1951, 6b, 336.

¹³ Schwarz and Gregor, *Z. anorg. Chem.*, 1939, 241, 1. Schwarz and Pflugmacher, *Ber.*, 1942, 75, 1062.

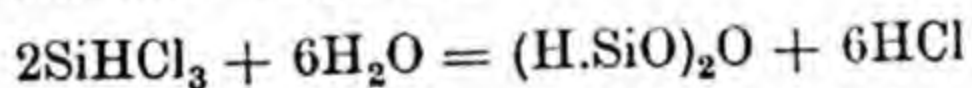
hydrolysed. Their structures probably consist of long chains of silicon atoms, with double bonds in the monohalides, but there is as yet no record of their X-ray examination. The formation of such compounds is a new and highly interesting aspect of silicon chemistry. The oxychlorides and oxybromides of silicon,¹⁴ which constitute a long series, the highest identified member of which is $\text{Si}_7\text{O}_6\text{Cl}_{16}$, differ fundamentally in that their structures are based on the Si—O—Si linkage.

Siloxene and Related Compounds.—Hydrolysis of the silicon halides and their alkyl or aryl substitution products gives rise to very interesting products, a number of which (the silicones) are now of major technical importance (*vide infra*). The structural feature common to them all is the *intermolecular* elimination of water between molecules of the initial hydrolysis products, forming larger molecules containing the Si—O—Si linkage.



In the analogous carbon compounds hydrolysis is less easy and if water is eliminated the process occurs intramolecularly.

Hydrolysis of silicon tetrachloride, followed by dehydration, leads to silica, which may be regarded as a three-dimensional assembly of silicon atoms joined by oxygen bridges of the above type. Silico-chloroform reacts with ice-cold water to form the unstable polymeric silicoformic anhydride

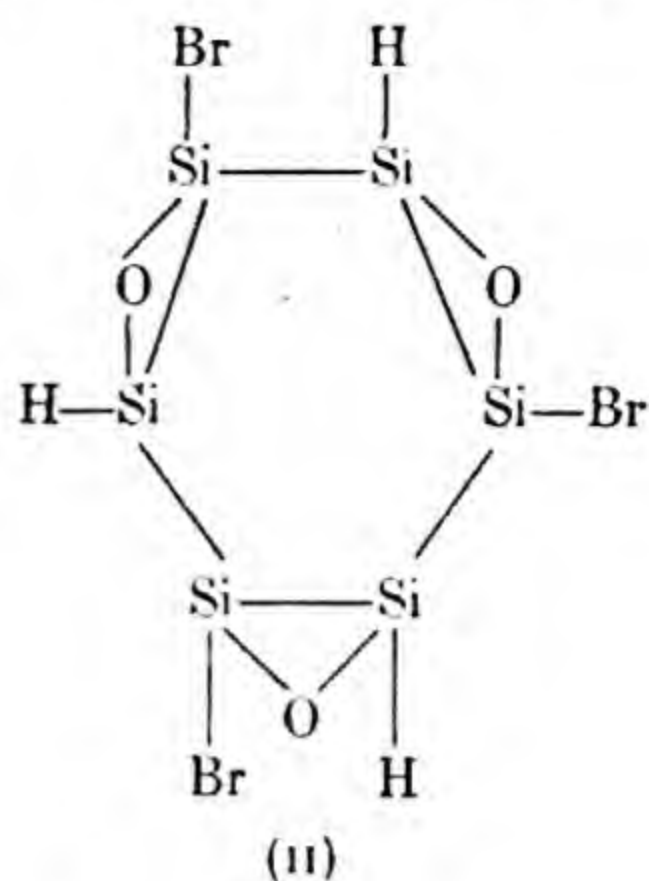
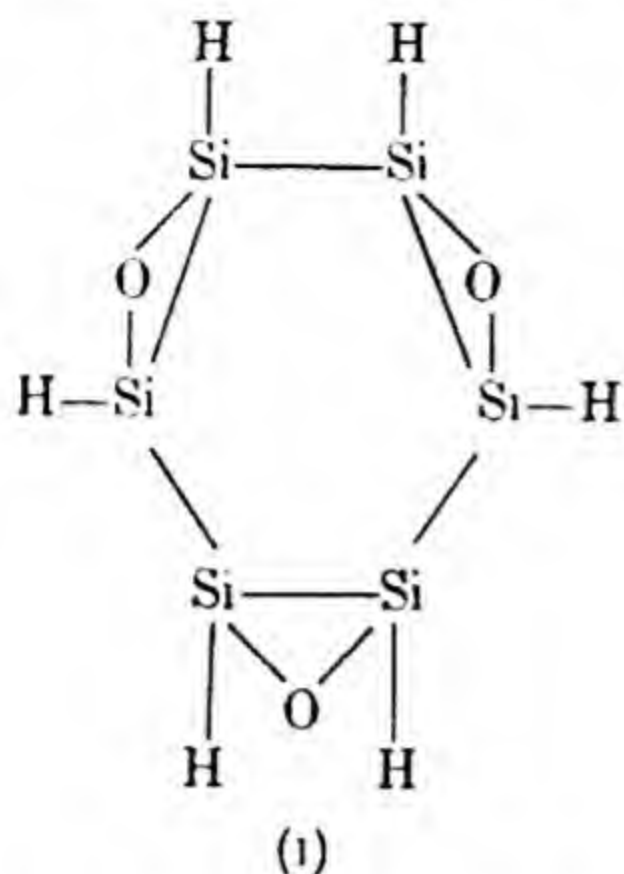


Hexachlorodisilane, Si_2Cl_6 , and octachlorotrisilane, Si_3Cl_8 , form respectively on controlled hydrolysis silico-oxalic acid and silico-mesoxalic acid, both of which are polymerized solids, the structures of which are not known, though it is extremely likely that they also contain silicon atoms joined by oxygen bridges.

Closely allied in structure to the above are siloxene and its derivatives, which have been exhaustively studied by Kautsky and his co-workers.¹⁵ If calcium silicide, CaSi_2 , is treated with a mixture of hydrochloric acid and alcohol, hydrogen is evolved and a white solid with the empirical formula $\text{Si}_2\text{H}_2\text{O}$ remains. This was named siloxene by Kautsky. It is spontaneously inflammable in air and a powerful reducing agent. The cyclic structure (I) below has been assigned to it.

¹⁴ Schumb and Klein, *J. Amer. Chem. Soc.*, 1937, 59, 261. Schumb and Holloway, *ibid.*, 1941, 63, 2753.

¹⁵ Kautsky and Herzberg, *Ber.*, 1924, 57, 1665.



Calcium silicide has a layer lattice with the calcium atoms arranged in sheets between sheets of combined silicon atoms. The action of the acid is believed to be to dissolve out the metal atoms, leaving the silicon sheets with oxygen and hydrogen atoms attached to their faces. Structure (I) must therefore be considered as extending indefinitely in the plane of the paper, with perhaps oxygen bridges between the structural units. This structure is speculative and unsupported by X-ray work.

Siloxene reacts with halogens, with partial or complete replacement of the hydrogen atoms.¹⁶ In the product we may envisage a new structural unit such as (II). The halogen compounds are transformed by water into hydroxy derivatives, the colour of which deepens from yellow to black as the number of (OH) groups is increased. Treatment of the hydroxyl derivatives with acids leads to the introduction of acidic groups (e.g. Cl, Br, CH_3CO_2) into the siloxene nucleus. The action of ammonia or of amines on the halogenated siloxenes also yields a series of amino or alkyl amino derivatives.¹⁷ Complete chlorination or bromination breaks down the compound to the oxyhalides $(\text{SiCl}_3)_2\text{O}$ or $(\text{SiBr}_3)_2\text{O}$.

The oxidation of siloxene either with air or potassium permanganate gives rise to an interesting chemiluminescence. Siloxene and its derivatives are flaky substances with a high adsorptive power. If a fluorescent dyestuff such as rhodamine is adsorbed either on the parent substance or on a product of its partial oxidation, permanganate oxidation gives a luminescence, the spectrum of which is identical with the fluorescence spectrum of the dyestuff employed. In this case it appears that the energy of the oxidation

¹⁶ Kautsky and Hirsch, *Z. anorg. Chem.*, 1928, **170**, 1.

¹⁷ Kautsky, *Ber.*, 1931, **64**, 1610.

reaction is handed on and used to excite fluorescence in the adsorbed molecules.

The Silicones.—This term is applied to a group of organo-silicon compounds derived from alkyl and aryl silicon halides by hydrolysis and the intermolecular elimination of water. They are thus related to the compounds described in the preceding section, though their structures are much better known. Their discovery is closely bound up with the classical work of Kipping and his school, which, however, covered a very much wider field of organo-silicon chemistry.¹⁸ In discussing the silicones it is first necessary to consider how the organo-silicon halides are prepared and hydrolysed and then the characterization and properties of the condensed hydrolysis products.

The intermediates, alkyl and aryl silicon halides, may be prepared by the following methods:

- (1) Reaction of a silicon halide with a metal alkyl (*e.g.* $\text{SiCl}_4 + \text{Hg}(\text{C}_6\text{H}_5)_2 = \text{Si}(\text{C}_6\text{H}_5)\text{Cl}_3 + \text{Hg}(\text{C}_6\text{H}_5)\text{Cl}$).
- (2) Use of the Grignard reagent (*e.g.* $\text{SiCl}_4 + \text{MgMeI} \rightarrow \text{SiMeCl}_3$, SiMe_2Cl_2 and SiMeCl_3).
- (3) Reaction of an aryl or alkyl halide with a Cu-Si or Ag-Si alloy.
- (4) Reaction of silicon and alkyl halides with Zn or Al.

The first two methods, and a number of variants of them which have been discovered, are largely of academic interest. The Grignard method, however, is very widely applicable and could be used for the large-scale production of intermediates. It has the disadvantage that it always gives a mixture of products. In the preparation of the methyl silicon chlorides, which are of particular importance, the products are MeSiCl_3 (b.p. 66°), Me_2SiCl_2 (b.p. 70°), Me_3SiCl (b.p. 57.6°) and, under suitable conditions, Me_4Si (26°). The separation of these requires very efficient fractionation.

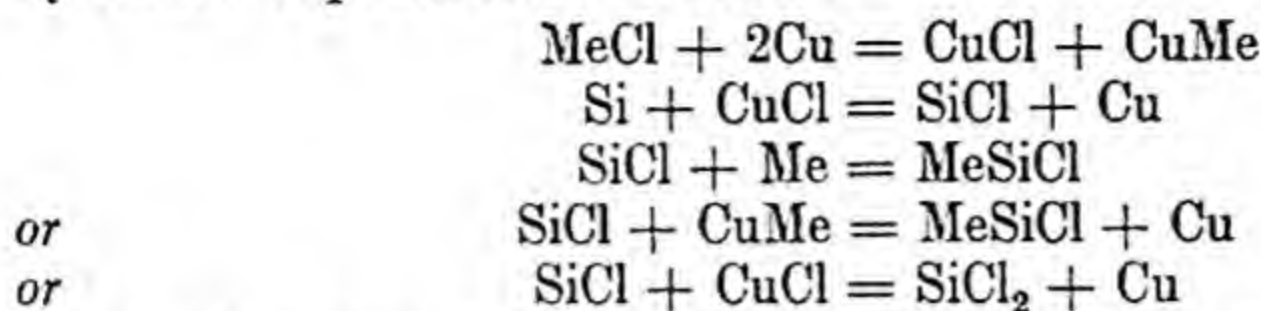
The direct synthesis of organo-silicon halides was first achieved by Rochow in 1945.¹⁹ Taking the preparation of methyl silicon chlorides as an example, methyl chloride vapour is passed over a copper-silicon mixture at *ca.* 300° . The latter is prepared by mixing the powdered elements (10 per cent Cu), pressing them, and sintering in an atmosphere of hydrogen at 1000° . In this reaction the main products are Me_2SiCl_2 and MeSiCl_3 .

The mechanism of the reaction is believed to involve the inter-

¹⁸ The late Professor Kipping's work is summarized in his Bakerian Lecture to the Royal Society (*Proc. Roy. Soc.*, 1937, 159, 193). For a detailed review of the chemistry of the silicones, see Rochow, *An Introduction to the Chemistry of the Silicones* (John Wiley and Sons, Inc., New York: Chapman and Hall, Ltd., London, 1951), see also Hardy and Megson, *Quart. Rev. Chem. Soc.*, 1948, 2, 25.

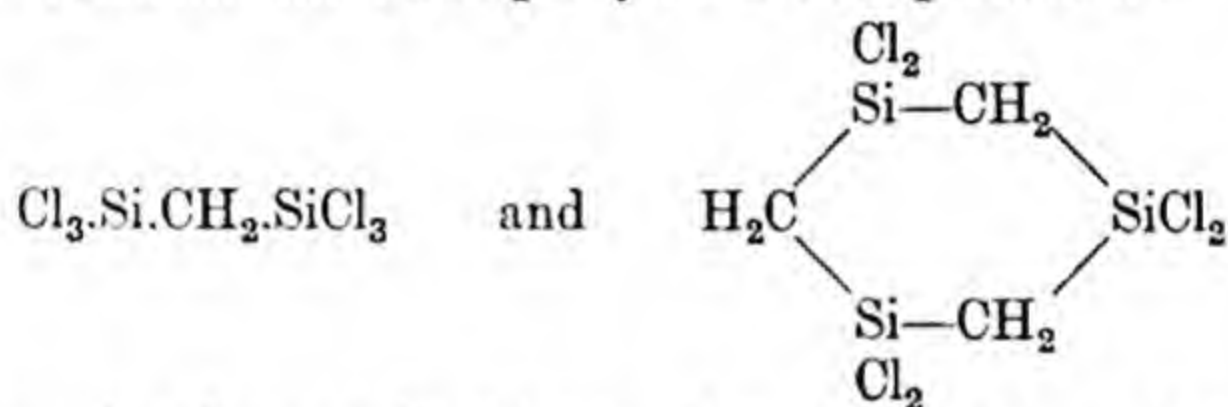
¹⁹ *J. Amer. Chem. Soc.*, 1945, 67, 963.

mediate formation of copper methyl, a hypothesis which is supported by other experimental evidence.



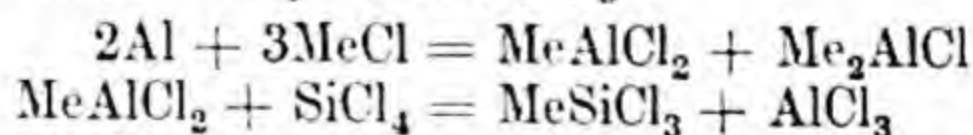
Thus, if methyl chloride vapour is passed at a low pressure and high streaming rate over copper at 250° and then over a lead mirror, a copper mirror is formed downstream from the heated zone and the lead mirror is removed (as PbMe_4). If methyl chloride vapour is passed over heated films of copper and silicon deposited side by side on a glass plate, the silicon is attacked only when the plate is so placed that the streaming methyl chloride has just passed over the copper.²⁰

The reaction with copper-silicon occurs with other alkyl monohalides and with halides containing more than one chlorine atom. Methylene chloride for example yields two products:



The process is also applicable to the preparation of vinyl- and alkyl-chlorosilanes.²¹ Silver has been recommended as a catalyst for forming aryl silicon halides by this method, and metals such as nickel, tin, antimony, manganese and titanium are also active, though there is at present no indication that they function by a similar mechanism.

The fourth method involves passing the alkyl and silicon halide vapours over finely divided zinc or aluminium at $300\text{--}500^\circ$. In this case the reaction mechanism is believed to entail the intermediate formation of a metal alkyl halide, *e.g.*

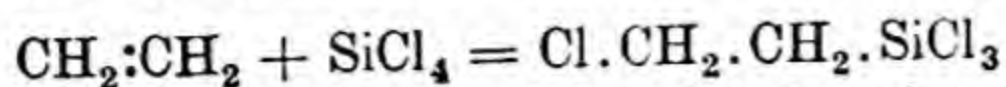


There are also methods whereby silicon tetrachloride may be made to react directly with certain hydrocarbons. Ethylene, for example, reacts with silicon tetrachloride under high pressure in presence of metallic chlorides or oxychlorides:²²

²⁰ Hurd and Rochow, *J. Amer. Chem. Soc.*, 1945, **67**, 963.

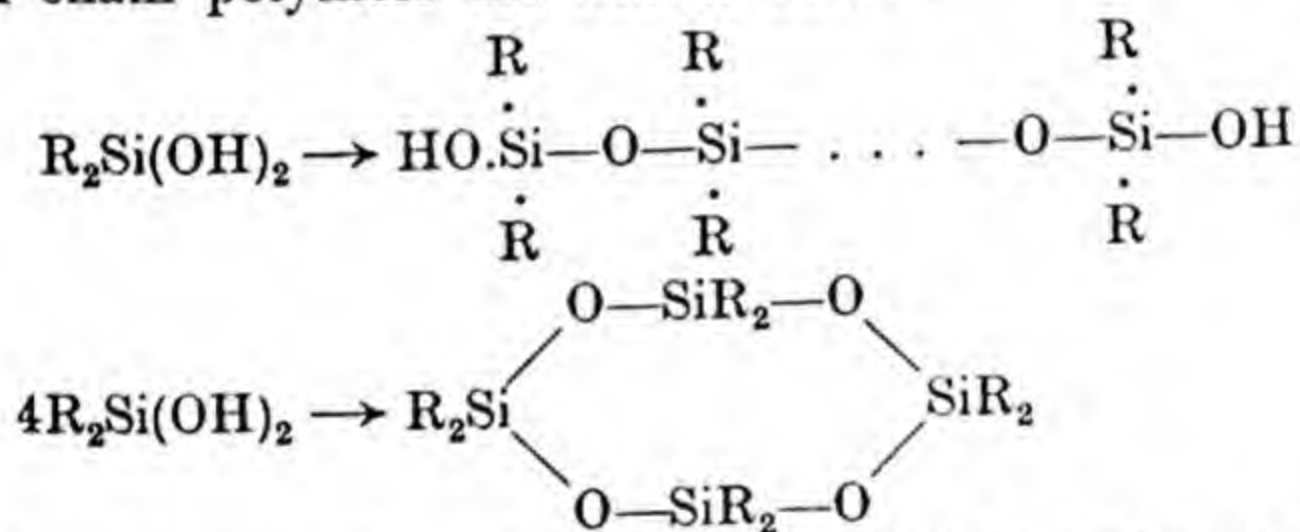
²¹ Hurd, *ibid.*, 1945, **67**, 963.

²² Shtetter, Russian Cert. of Invention 44934, 1935. See Hardy and Megson, *Quart. Rev. Chem. Soc.*, 1948, **2**, 28.

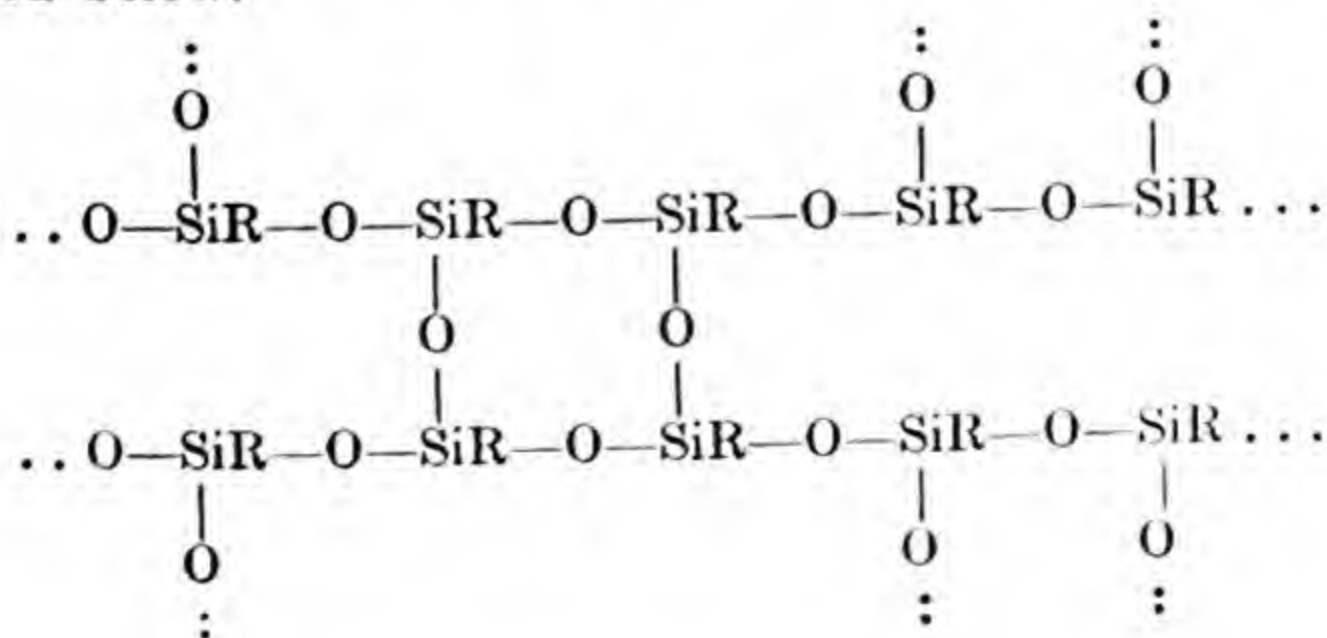


This type of synthesis, if it could be developed to produce compounds such as Me_2SiCl_2 , would be of great value because it would eliminate the use of intermediates such as methyl chloride.

The rate of hydrolysis of aryl and alkyl silicon halides is slower than that for silicon tetrachloride, but requires careful control of the conditions. The products are silanols (*e.g.* $\text{Me}_3\text{SiCl} \rightarrow$ trimethyl silanol, $\text{Me}_3\text{Si}(\text{OH})$, b.p. 98.6°). They condense readily to the corresponding disiloxanes ($2\text{R}_3\text{SiOH} \rightarrow \text{R}_3\text{Si}.\text{O}.\text{SiR}_3$). When two halogen atoms are present in the molecule, more complex products often result because of the great ease with which the hydrolysate loses water. Dimethylsilicon dichloride, for example, gives a colourless oil with the empirical formula $\text{C}_2\text{H}_6\text{SiO}$, containing roughly equal amounts of linear diol polymers of the type $\text{HO}.\text{SiMe}_2(\text{OSiMe}_2)_n\text{OSiMe}_2\text{OH}$ and of more volatile cyclic polymers containing from 3 to 9 units in the ring. (It may be noted in passing that the term silicone was applied originally to this group of compounds when it was thought that they were analogous to ketones and were formed by intramolecular eliminations of water). Typical ring and chain polymers are shown below:

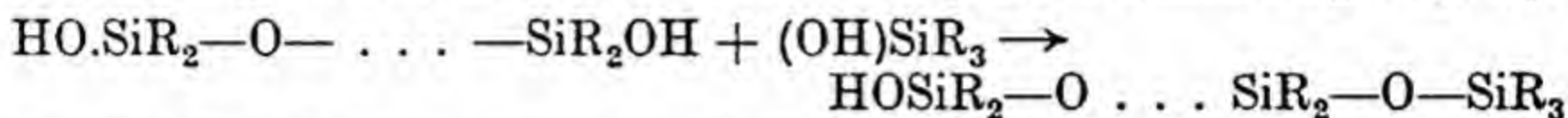


Trifunctional organosilicon intermediates (RSiX_3) when hydrolysed form solid products of much greater complexity, in which there is cross linking, made possible by the three (OH) groups attached to silicon in the original hydrolysate. This type of structure is illustrated below.



With aromatic derivatives water is in general less readily eliminated and, although it is impossible to isolate the diol $\text{Me}_2\text{Si}(\text{OH})_2$, the corresponding phenyl derivative $\text{Ph}_2\text{Si}(\text{OH})_2$ may readily be prepared. It is, however, condensed by heating.

The characteristic modes of condensation of the three types of silicols are often combined in practice. Thus if R_2SiCl_2 is mixed with a certain amount of R_3SiCl before hydrolysis, the R_3SiOH will check the growth of chains since it has only one functional group, *e.g.*



Similarly, SiCl_4 or a compound of the type RSiCl_3 may be added to produce a controlled amount of cross linking. Condensation does not always develop to the full extent at room temperature and by heating the initial product further water is usually eliminated, and the silicone becomes more complex. Controlled oxidation brings about the same result, since for each alkyl or aryl group so removed a potential new Si—O—Si link is created.

Another important general principle is that the addition of a small amount of concentrated sulphuric acid to a condensed silicone

tends to open up the $\begin{array}{c} \diagup \\ \text{Si—O—Si} \\ \diagdown \end{array}$ linkages, probably by the

formation of unstable esters $\left(\begin{array}{c} \diagup \\ \text{Si—HSO}_4 \\ \diagdown \end{array} \right)$. These undergo hydrolysis and reform polymerized molecules. If this treatment is applied to a mixture of linear and cyclic polymers from Me_2SiCl_2 mixed with some $\text{Me}_3\text{Si—O—SiMe}_3$, the result is that the cyclic polymers tend to break down into linear polymers with terminal —SiMe_3 groups.

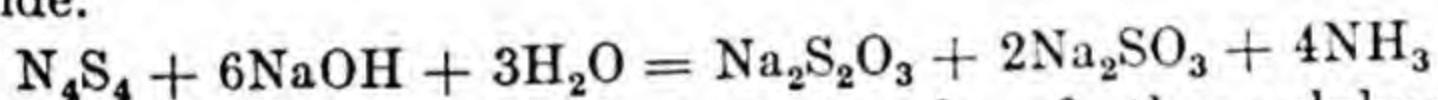
Silicones have found limited applications as water-repellents, lubricants, greases, resins, rubbers, and in hydraulic systems. The water-repellent property is due to the tendency of a surface film to present a hydrocarbon layer to the outer atmosphere. The additional properties which are useful in lubricants, greases and resins are the high thermal stability, low volatility, and, in some applications, the good electrical insulating properties. The rubbery silicones, which are made by suitably blending the constituents to give a proper measure of cross linking, have the above properties and retain their elastic properties at much lower temperatures than natural rubbers. The silicone fluids, in which the degree of condensation has been limited, can be made with a wide range of viscosity and molecular complexity. They are thermally stable and the viscosity changes little with temperature. They combine most of the properties already mentioned and have been used, *inter*

alia, in hydraulic systems, shock absorbers, and in the construction of electrical condensers.

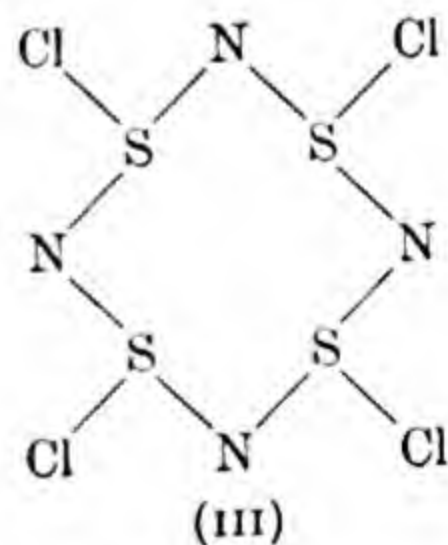
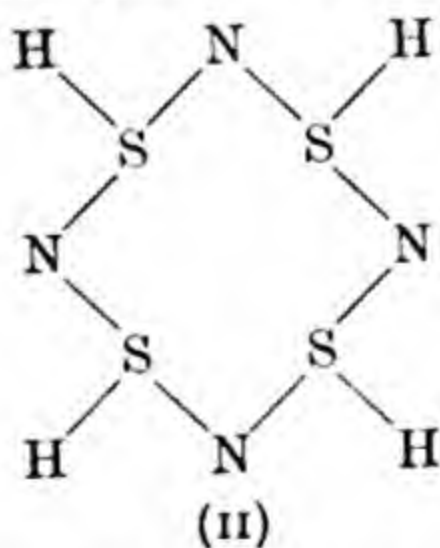
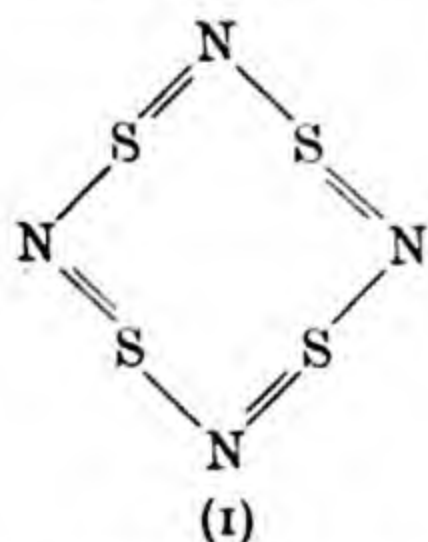
The Nitrogen Sulphides.

Nitrogen forms a series of compounds with sulphur which present some exceedingly interesting structural problems. The best known of these compounds, N_4S_4 , is commonly referred to as nitrogen sulphide, although its reactions are those of a sulphur nitride. It may be obtained directly from sulphur and ammonia ($10S + 4NH_3 = N_4S_4 + 6H_2S$), but is better prepared by the reaction of ammonia with sulphur chloride ($S : Cl, 1 : 3-4$) in benzene.²³ It forms orange crystals which sublime readily near the melting-point (178°). The compound is endothermic and may explode when heated, or on shock. It is soluble in benzene and carbon disulphide and the molecular weight has been established in these solutions.

The structure of N_4S_4 was for some time very uncertain. On alkaline hydrolysis, ammonia is produced and not hydrogen sulphide.



Under milder conditions of hydrolysis salts of other sulphur acids are formed.²⁴ This reaction is what would be expected from a nitride rather than a sulphide. No hydrazine is formed on reduction, showing that the nitrogen atoms in the molecule are probably not joined. It is also probable that the sulphur atoms are not directly linked, since reaction with secondary alkylamines converts all the sulphur into the thiodiamine $Alk_2N-S-NAlk_2$. These facts are best expressed by the cyclic structure (I).



Electron diffraction results²⁵ confirm the chemical evidence and

²³ For details of this and other methods of preparation, see Yost and Russell, *Systematic Inorganic Chemistry of the Fifth-and-Sixth Group Nonmetallic Elements* (New York, Prentice-Hall, Inc., 1944).

²⁴ Goehring, *Ber.*, 1947, 80, 110.

²⁵ Lu and Donohue, *J. Amer. Chem. Soc.*, 1944, 66, 818.

give an N—S distance of 1.62 Å., the distances calculated from covalent bond radii being: N—S, 1.74; N=S, 1.54 Å. This indicates that all the linkages are alike and intermediate in character between single and double bonds. The ring in (I) is puckered.

Nitrogen tetrasulphide undergoes a number of interesting reactions, the most significant of which are its reduction to $\text{N}_4\text{S}_4\text{H}_4$ (II) by stannous chloride in a benzene-alcohol mixture, and its reaction with chlorine when suspended in carbon disulphide to form $\text{N}_4\text{S}_4\text{Cl}_4$ (III). It is very probable that the addition in these compounds occurs on the sulphur atom. Thus the hydrogen derivative resists fairly strong alkalis, which would be unlikely if N—H groups were present, and also gives with formaldehyde the compound $(\text{NS}.\text{CH}_2\text{OH})_4$. Had the hydrogen been attached to nitrogen the compound $\text{SN}.\text{CH}_2\text{NS}$ would have been expected since diethylamine with the same reagent gives $(\text{C}_2\text{H}_5)_2\text{N}.\text{CH}_2.\text{N}(\text{C}_2\text{H}_5)_2$.

On refluxing N_4S_4 with acetyl chloride the compound $\text{N}_3\text{S}_4\text{Cl}$, thiotrithiazyl chloride, is formed. This is a salt of the $(\text{N}_3\text{S}_4)^+$ radical and by double decomposition reactions other salts are obtained (*e.g.* $\text{N}_3\text{S}_4\text{NO}_3$, $\text{N}_3\text{S}_4\text{I}$, $\text{N}_3\text{S}_4\text{HSO}_4$).

The nitrogen sulphide of the formula NS_2 , which is formed by subliming N_4S_4 with sulphur at 125° ,²⁶ is a red liquid which may be the analogue of NO_2 , although there is no direct evidence of its structure. The unstable compound N_2S_5 , formed by heating N_4S_4 with carbon disulphide at 100° , may also correspond to N_2O_5 , but again no structural evidence is available. A nitrogen selenide $(\text{N}_4\text{Se}_4)_x$ is obtained by the action of dry ammonia on methyl or ethyl selenite dissolved in benzene: ²⁷ it is highly explosive and has not been studied in any detail. The tellurium compound Te_3N_4 , formed by the prolonged action of liquid ammonia on tellurium bromide,²⁸ is likewise unstable.

Phosphorus Chloronitride and Related Compounds.²⁹

The phosphorus chloronitrides are a group of compounds of the composition $(\text{PNCl}_2)_n$, formed by various methods, the earliest of which was the reaction of gaseous ammonia with phosphorus pentachloride. This gives low yields and better results are obtained by heating phosphorus pentachloride and ammonium chloride in sealed tubes at 120° , or by refluxing these two reactants in tetrachloroethane (b.p. 146.3°), distilling off the solvent, and fractionally

²⁶ Usher, *J.C.S.*, 1925, 730.

²⁷ Strecker and Schwarzkopf, *Z. anorg. Chem.*, 1934, 221, 193.

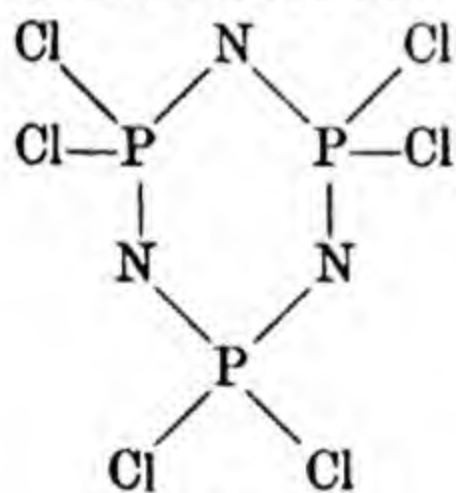
²⁸ Strecker and Mahr, *ibid.*, 1934, 221, 199.

²⁹ For a detailed review of this topic, see Audrieth, Steinman and Toy, *Chem. Rev.*, 1943, 32, 109.

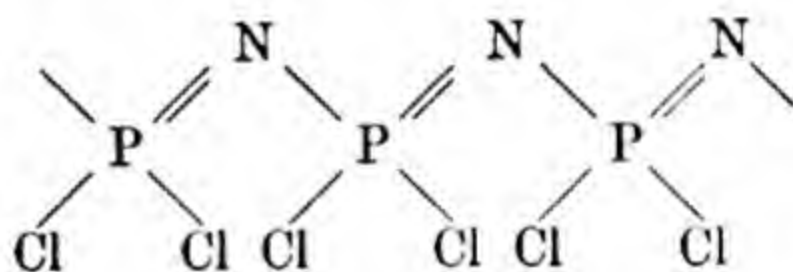
distilling the residue. A similar reaction occurs between phosphorus pentabromide and ammonium bromide.

These reactions give a mixture of products, the chief components of which are the trimer $(\text{PNCl}_2)_3$ (m.p. 114° ; b.p. $127^\circ/13$ mm.) and the tetramer $(\text{PNCl}_2)_4$ (m.p. 123.5 ; b.p. $188^\circ/13$ mm.), but smaller amounts of $(\text{PNCl}_2)_5$, $(\text{PNCl}_2)_6$ and $(\text{PNCl}_2)_7$ may also be isolated. All of these polymers are soluble in benzene, in which molecular weights have been determined. During the separation by distillation a good deal of material is lost by further polymerization, and this limits the applicability of the distillation method, but it is possible that other methods will be found whereby higher polymers can be isolated. The monomer and dimer have not been prepared. At 250 – 350° the phosphorus chloronitrides are converted to an insoluble rubber-like polymer, which swells reversibly in benzene. The change in its X-ray diffraction pattern on stretching is similar to that which occurs in stretched natural rubber. This effect is probably due to orientation of long-chain polymers (II, below) in the direction of stretch.

The trimer $(\text{PNCl}_2)_3$ has been shown by electron diffraction measurements³⁰ to have a structure consisting of a plane ring (I), whilst the tetramer forms a puckered ring. The structures of these two compounds have also been studied by the X-ray method. The



(I)



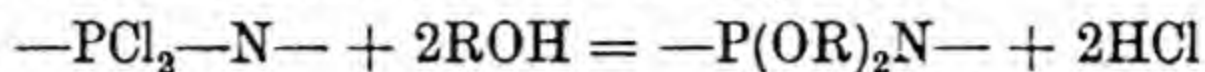
(II)

most significant point about the bond lengths is that all the P—N bonds are the same, which suggests that there is resonance in these molecules just as there is in benzene. The P—N bond length corresponds to 50 per cent double bond character. Ionic structures probably also contribute to the resonance.

The phosphorus chloronitrides are rather resistant to hydrolysis, but they react with water in ether solution with replacement of Cl by OH. More vigorous hydrolytic reagents give ammonia and phosphoric acid. Hydrolysis of the trimer in ether gives the two compounds $\text{P}_3\text{N}_3\text{Cl}_4(\text{OH})_2$ and $\text{P}_3\text{N}_3(\text{OH})_6$, which are acidic and yield well-defined salts (*e.g.* $\text{P}_3\text{N}_3\text{O}_6\text{Ag}_6$). The halogen atoms

³⁰ Brockway and Bright, *J. Amer. Chem. Soc.*, 1943, 65, 1551.

may be replaced partly or completely by NH_2 groups by reaction with ammonia, products such as $\text{P}_3\text{N}_3\text{Cl}_4(\text{NH}_2)_2$ being obtained. A similar reaction occurs with amines, aniline, for example, giving the compound $\text{P}_3\text{N}_3(\text{NHPh})_6$ with the trimer.³¹ There is also an analogous reaction with alcohols and phenols:



The trimer and tetramer undergo a Friedel-Crafts condensation with benzene in presence of aluminium chloride, giving products with phenyl groups attached to the phosphorus atoms. A similar reaction occurs with Grignard reagents and organometallic compounds, phenyl magnesium bromide giving with the tetramer two isomeric tetraphenyl derivatives in which the four substituted groups are on adjacent and opposite phosphorus atoms.³² The formation of two isomeric octaphenyl derivatives has also been claimed, but no reason has been advanced to account for the occurrence of isomers in this case.

Schmitz-Dumont and his co-workers³³ have studied the replacement of chlorine by fluorine and have found that this occurs readily with mild reagents such as lead fluoride. One of the most interesting points in this work is the formation of the compound $\text{P}_4\text{N}_4\text{Cl}_2\text{F}_6$, a derivative of the tetramer, as one of the reaction products from PbF_2 and the trimer $\text{P}_3\text{N}_3\text{Cl}_6$.

Preparation of Fluorine.

During the last twenty-five years there have been major developments in the production of elementary fluorine. The preparation by Moissan's original method entailed the use of a platinum or copper cell with platinum-iridium electrodes, and an electrolyte consisting of anhydrous hydrogen fluoride and potassium fluoride in roughly a 12:1 molecular ratio. With this electrolyte it is necessary to cool the cell to about -30° to avoid excessive vaporization of hydrogen fluoride, and the method has been completely abandoned. In its place two types of cell are now used:³⁴

- (1) The medium temperature cell, which operates at $70-100^\circ$ with an electrolyte of the composition $\text{KF} \cdot 2-3\text{HF}$.
- (2) The high temperature cell, which operates at $250-270^\circ$ with an electrolyte of the composition $\text{KF} \cdot \text{HF}$.

A number of laboratory cells of these two types have been described,

³¹ Bode, Butow and Lienau, *Ber.*, 1948, 81, 547.

³² Bode and Thamer, *Ber.*, 1943, 76, 121.

³³ Schmitz-Dumont and Kulkens, *Z. anorg. Chem.*, 1938, 238, 189; Schmitz-Dumont and Brasches, *ibid.*, 1939, 243, 113.

³⁴ For a review of the laboratory and technical production of fluorine, see Leech, *Quart. Rev. Chem. Soc.*, 1949, 3, 22.

as well as cells suitable for technical operation. The constructional materials used have included copper, nickel, and magnesium, but either type of electrolyte can be handled in a cell made of mild steel. For the medium temperature cell the anode may be of nickel or, better, of carbon, and the cathode of steel, while in the high temperature cell a graphite anode and a steel or copper cathode are used. The diagram below shows the construction of a medium temperature cell suitable for laboratory use.

The use of fluorine in the laboratory is beset with fewer difficulties than is commonly supposed, although considerable care is necessary on account of the high reactivity. Many organic substances burn

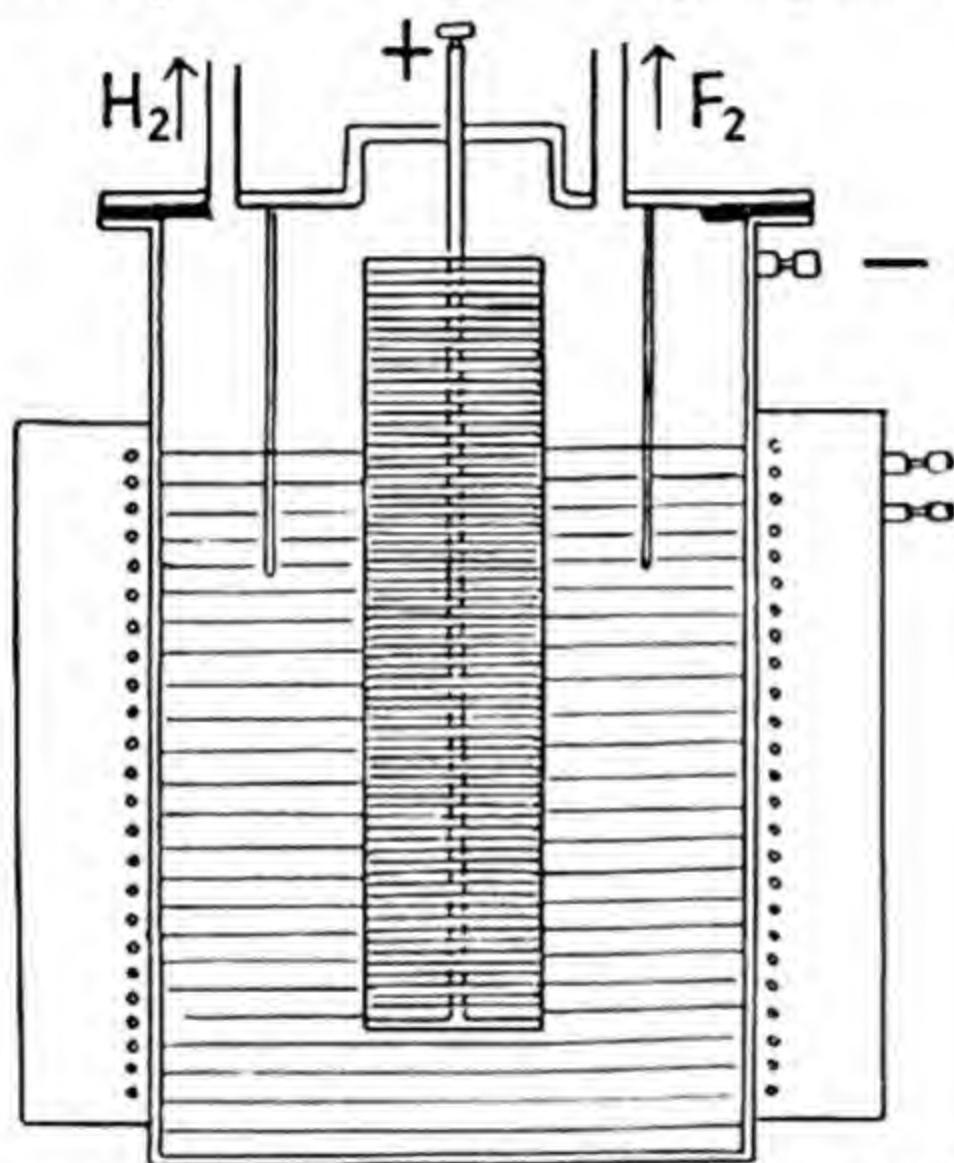
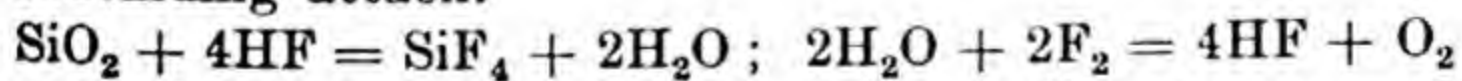


FIG. 55.—Electrically heated, medium temperature fluorine cell with carbon anode.

in it and contact with grease must be avoided. There is, however, no appreciable reaction at room temperature with metals such as steel, copper, and nickel, and these may be used in constructing apparatus and leads. There is also little reaction with Pyrex glass or fused silica, provided the gas is free from hydrogen fluoride. The latter undergoes the following cycle of reactions, which result in a continuing attack.



Hydrogen fluoride may be removed by cooling to *ca.* -80° , at which temperature fluorine (b.p. -188°) is volatile whereas hydrogen fluoride (b.p. 19.5°) condenses. It may also be removed by contact with sodium fluoride, which forms the acid fluoride $\text{NaF} \cdot \text{HF}$ but does not react with fluorine.

Fluorides of Carbon.

The fluorides of carbon form a large group of compounds which parallel the hydrocarbons in structure and, to a certain extent, in physical properties. They are known collectively as fluorocarbons and the analogues of the saturated hydrocarbons are very inert. The simplest fluorocarbon, CF_4 , was prepared in an impure state by Moissan in 1890, but was first obtained pure by Lebeau and Damiens in 1926.³⁵ Four years later Ruff and Keim³⁶ prepared CF_4 , C_2F_4 , C_2F_6 and C_3F_8 by the reaction of fluorine with carbon. In this reaction small amounts of higher homologues of the series $\text{C}_n\text{F}_{2n+2}$ are also formed. Reaction of graphite with fluorine at 200° leads to the interstitial fluoride $(\text{CF})_n$ (see p. 487) and this also breaks down at higher temperatures to a mixture of fluorocarbons.

The preparation of more complex fluorocarbons by the direct reaction of hydrocarbons with fluorine is unsatisfactory as the reactions are highly exothermic and partial or complete breakdown of the carbon skeleton of the hydrocarbon molecule usually occurs. It is necessary to moderate the reaction, which may be done:

- (a) By dilution of the fluorine with nitrogen, cooling, and carrying out the reaction in a relatively inert solvent such as carbon tetrachloride.
- (b) By catalytic fluorination. Usually the hydrocarbon vapour is mixed with a stream of fluorine diluted with nitrogen, in a reaction tube packed with gold- or silver-plated copper gauze and heated to $100\text{--}300^\circ$, according to the reaction under investigation.
- (c) By passing the vapour of the organic compound to be fluorinated over cobalt trifluoride heated to $100\text{--}300^\circ$. The cobaltic fluoride is preformed in the reactor by treating cobaltous fluoride with fluorine and may be similarly regenerated for conversion of a further batch of hydrocarbon. The essential reaction is $\text{>CH}_2 + 4\text{CoF}_3 = \text{>CF}_2 + 2\text{HF} + 4\text{CoF}_2$. The catalytic method (b) probably also depends on the intermediate formation of auric or argentic fluoride.

These methods have been applied successfully to the replacement of hydrogen by fluorine in a wide variety of aliphatic and aromatic compounds. There are, in addition, a number of methods for producing partly fluorinated compounds, the most important of which is the Swarts reaction. In this, organic halogen compounds are treated with antimony trifluoride in presence of a pentavalent antimony halide, or, in certain cases, with hydrogen fluoride and

³⁵ *Compt. rend.*, 1926, 182, 1340.³⁶ *Z. anorg. Chem.*, 1930, 192, 249.

antimony trifluoride. Examples of this reaction are the conversion of CCl_4 to CCl_3F , CCl_2F_2 and CClF_3 and of $\text{C}_6\text{H}_5\text{CCl}_3$ to $\text{C}_6\text{H}_5\text{CF}_3$. It is also applicable to the production of mixed halides of other elements (*e.g.* SiClF_3 , etc., and POClF_2 , etc.).

The boiling-points of fluorocarbons are close to those of the hydrocarbons, as is shown by the following data for the aliphatic series $\text{C}_n\text{H}_{2n+2}$ and $\text{C}_n\text{F}_{2n+2}$.

$n =$	1	2	3	4	5	6	8	16
Fluorocarbon . . .	-128°	-78°	-38°	-0.5°	22°	51°	104°	240°
Hydrocarbon . . .	-161°	-88°	-44°	-0.5°	36°	68°	125°	286°

The inertness of the fluorocarbons makes them potentially useful as solvents, lubricants and as insulators. The mixed chlorofluoro hydrocarbons, prepared by the Swarts reaction and usually known collectively as the Freons, are also widely used in refrigeration. They offer a suitable range of boiling-points (*e.g.* CF_2Cl_2 , b.p. -30°), have good thermodynamic properties, and are non-toxic and non-corrosive. A related compound which is also important technically is polytetrafluoroethylene $(\text{C}_2\text{F}_4)_n$, which is a white solid with good electrical insulating properties and outstanding resistance to chemical attack. It is, for example, unattacked by boiling aqua regia and is an excellent material for gaskets in chemical plant. It is made by cracking the Freon CHClF_2 at 800° ($2\text{CHClF}_2 = \text{C}_2\text{F}_4 + 2\text{HCl}$) and polymerizing the monomeric tetrafluoroethylene under pressure in contact with an aqueous solution of a persulphate.

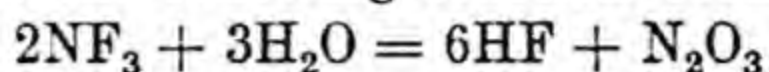
The detailed chemistry of organic fluorine compounds contains a great many points of outstanding interest, but lies outside the scope of this chapter. Two points may be mentioned to illustrate the intriguing differences between hydrocarbon and fluorocarbon chemistry. The first concerns the amine $\text{N}(\text{CF}_3)_3$, one of the products of the fluorination of trimethylamine with cobaltic fluoride, which is inert and devoid of basic properties. The second concerns the compound CF_3I which behaves as a positive iodine compound, yielding CF_3H and not CF_3OH on hydrolysis. It has also proved possible to prepare from CF_3I organometallic compounds such as HgCF_3I , $\text{Hg}(\text{CF}_3)_2$, $\text{P}(\text{CF}_3)_3$ and $\text{As}(\text{CF}_3)_3$.

Fluorine Compounds of Elements of Group V B.

The anomalous type of behaviour of the carbon fluorides is also encountered to some extent in the fluorides of other non-metallic elements. Those of boron (BF_3 , b.p. -101°) and silicon (SiF_4 , b.p. -96° ; Si_2F_6 , b.p. -19°) call for no special comment as they resemble the other halides in their reactivity, except that they

form the acids HBF_4 and H_2SiF_6 . They are also considerably more volatile than the other halides of these two elements.

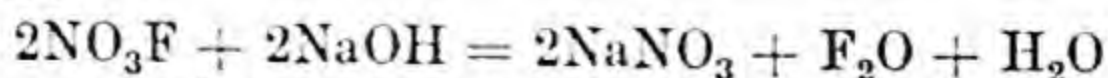
Nitrogen trifluoride (b.p. -119°), which was first prepared in 1928 by electrolysing fused anhydrous ammonium hydrogen fluoride, NH_4HF_2 , at 125° ³⁷ is remarkable because of its inertness. It is unchanged by contact with liquid water, though when sparked with water vapour the following reaction occurs:



It is also unaffected by alkalis and acids, and may be heated to moderate temperatures with metals without reaction. A mixture with hydrogen explodes when sparked, and nitrogen and hydrogen fluoride are formed. This behaviour contrasts sharply with the highly unstable nitrogen trichloride, which decomposes with water to form ammonia and hypochlorous acid. The fluoride is exothermic, with a heat of formation of 53 k.cals., whereas nitrogen trichloride is endothermic ($Q = -110.8$ k.cals.).

In the electrolytic preparation of nitrogen trifluoride small amounts of NH_2F and NHF_2 are produced, both of which are reactive. A third product, NF_2 , is also said to be formed, but has not been fully characterized. Another nitrogen fluoride, N_2F_2 , which is obtained by the decomposition of N_3F ,³⁸ has been shown by electron diffraction to have the constitution $\text{F}-\text{N}=\text{N}-\text{F}$, but has not yet been studied chemically. This is clearly a field where much remains to be done, especially when considered in relation to the fluorination of aliphatic amines, which yields not only inert products such as $\text{N}(\text{CF}_3)_3$, $\text{N}(\text{CF}_3)_2\text{F}$ and $\text{N}(\text{CF}_3)\text{F}_2$, but also nitrogen trifluoride itself.

The compounds nitrosyl fluoride, NOF , and nitroxyl fluoride, NO_2F , resemble their chlorine analogues closely. Fluorine, however, forms yet another compound, NO_3F , sometimes called fluorine nitrate, which has no chlorine analogue. It was first prepared by Cady³⁹ by the action of fluorine on 3-N nitric acid, and has since been made by fluorinating either pure nitric acid or metallic nitrates. It is an explosive gas (b.p. -45.9°) and the preparation is among the more hazardous operations of inorganic chemistry. It does not attack dry glass or quartz, but is decomposed by water into oxygen, fluorine monoxide, nitric acid and hydrogen fluoride. The reaction with 2 per cent aqueous sodium hydroxide is in accordance with the equation:



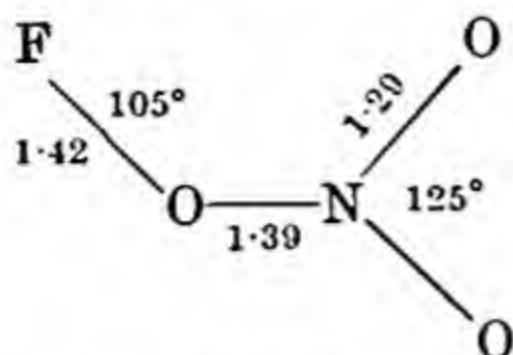
The structure, as determined by the electron diffraction method,

³⁷ Ruff, Fischer and Luft, *Z. anorg. Chem.*, 1928, **172**, 417.

³⁸ Bauer, *J. Amer. Chem. Soc.*, 1947, **69**, 3104.

³⁹ *Ibid.*, 1934, **56**, 2635.

shows a similarity to nitric acid, with the three oxygen atoms in the same plane as the nitrogen atoms. The dimensions given below are in Ångstrom units.



The fluorides of phosphorus, arsenic, antimony and bismuth call for little comment. Phosphorus forms a range of fluorides (PF_3 , PF_5 , POF_3) similar in most respects to the corresponding chlorides, except that PF_3 and POF_3 are rather more resistant to hydrolysis and that the donor properties of the phosphorus atom in PF_3 are less marked than in PCl_3 . Fluorine analogues of P_2Cl_4 and P_2I_4 have not yet been prepared.

Arsenic and antimony form reactive pentafluorides as well as trifluorides, but no pentachloride of arsenic is known, although SbCl_5 is readily obtained. In the case of bismuth the pentafluoride, which is produced by the action of fluorine on the trifluoride, is the only pentahalide known. It is also reactive and has been considered as a reagent for the fluorination of organic compounds.

Fluorine Compounds of Elements of Group VI B.

The fluorides of oxygen are discussed elsewhere (see p. 334). Sulphur, selenium and tellurium all form hexafluorides, which have no parallel among the other halides of these elements, and also lower fluorides. The formulæ and boiling-points of these are tabulated below:

	<i>b.p.</i> °		<i>b.p.</i> °		<i>b.p.</i> °
SF_6	— 63.8	SeF_6	— 46.6	TeF_6	— 38.9
S_2F_{10}	29	SeF_4	93		
SF_4	— 40				
S_2F_2	— 38.4				

The three hexafluorides are formed when the elements are burnt in fluorine, the decafluorides S_2F_{10} , Te_2F_{10} and probably also Se_2F_{10} being formed in small amounts simultaneously. The stability of sulphur hexafluoride resembles that of nitrogen fluoride. It is unaffected by water, acids, alkalis and a variety of metals and non-metals. Even sodium reacts only at temperatures well above its melting-point. The hexafluorides of selenium and tellurium are somewhat more reactive. For example, both react with mercury at room temperature. In the case of the tellurium compound, which is hydrolysed by water, the greater reactivity is understand-

able because the covalency maximum of the element is eight and is not therefore reached in the hexafluoride. The only decafluoride which has been studied in detail is S_2F_{10} , and this appears to be as inert as SF_6 . A very interesting extension of this field has arisen through the preparation of trifluoromethyl sulphur pentafluoride, CF_3SF_5 (b.p. -20.4°), by the fluorination of CH_3SH or CS_2 with cobaltic fluoride.⁴⁰ It was expected that CH_3SH would give CF_3SF , just as CH_3OH gives CF_3OF ,⁴¹ but the tendency for the maximum covalency to occur in fluorides evidently asserts itself in this instance also. The substituted sulphur hexafluoride is, as far as is known, about as inert as the hexafluoride: both are good electrical insulators and the hexafluoride has been used in the construction of high voltage generators.

The lower fluorides of sulphur, selenium and tellurium are all reactive and show a general resemblance to the other halides. There is still some uncertainty about the identity of the sulphur compounds, which may arise from the fact that they decompose in contact with glass, but it is fairly sure that SF_4 and S_2F_2 exist. So far the only lower fluorides of selenium and tellurium for which any evidence has been obtained are SeF_4 and TeF_4 , but it is extremely likely that others will be prepared in time.

Interhalogen Compounds.⁴²

The halogens form compounds with one another which are of four types, AB , AB_3 , AB_5 and AB_7 . None are at present known which contain more than two different halogens, although in the closely related polyhalide ions (*vide infra*) this does occur. The formulæ and boiling-points are tabulated below:

Type AB	Type AB_3	Type AB_5	Type AB_7
$ClF(-100^\circ)$	$ClF_3(12^\circ)$	$BrF_5(40^\circ)$	$IF_7(4^\circ)$
$BrF(20^\circ)$	$BrF_3(127^\circ)$	$IF_5(97^\circ)$	
$BrCl(5^\circ)$	$ICl_3(\text{decomp.})$		
$ICl(97.4^\circ)$			
$IBr(116^\circ)$			

All are obtained by the direct union of the elements. Chlorine and fluorine, for example, combine when passed in equimolecular proportions through a nickel tube at 200° . With excess fluorine at 280° the trifluoride results. Similarly bromine monofluoride is prepared

⁴⁰ Silvey and Cady, *J. Amer. Chem. Soc.*, 1950, **72**, 3624.

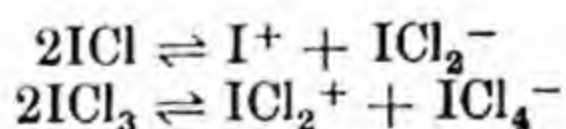
⁴¹ Kellog and Cady, *ibid.*, 1948, **70**, 3986.

⁴² For recent reviews of this topic, see Booth and Pinkston, *Chem. Reviews* 1947, **41**, 421. Sharpe, *Quart. Rev. Chem. Soc.*, 1950, **4**, 115.

by saturating bromine with fluorine at 10° . When bromine vapour carried by a stream of nitrogen is mixed with fluorine there is an exothermic reaction, the main product of which is bromine trifluoride. With excess fluorine at 200° the same reactants give bromine pentafluoride. Iodine burns in fluorine to form the pentafluoride, while if the pentafluoride is refluxed in a stream of fluorine through a tube heated to 200° the heptafluoride, IF_7 , is obtained. Pure bromine monochloride exists only at relatively low temperatures. Iodine mono- and trichlorides and iodine monobromide, on the other hand, all of which are formed by mixing the elements in the correct proportions, are more stable.

The reactions of the interhalogen compounds containing fluorine have not been studied in great detail, though all are highly reactive. Thus we find that most metals and non-metals either react explosively or burn in chlorine trifluoride and bromine trifluoride, the products being as a rule those which would be obtained in the reaction with fluorine. Organic compounds also react vigorously. The halogen fluorides also react violently with water and with chlorine trifluoride the compound ClOF has been obtained. Thionyl chloride and bromine trifluoride or iodine pentafluoride give thionyl chlorofluoride, SOClF . Carbon monoxide and chlorine monofluoride form carbonyl chlorofluoride, while with iodine pentafluoride and carbon monoxide, carbonyl iodofluoride, COIF , results. The formation of bromotetrafluorides (*e.g.* KBrF_4) from bromine trifluoride and metal fluorides and of the corresponding acids (*e.g.* SbBrF_6 , AuBrF_6) is referred to elsewhere (*see* p. 515). Iodine pentafluoride forms analogous compounds (*e.g.* KIF_6 , ISbF_{10}). The reactions of the interhalogens containing no fluorine are more familiar: they are much less reactive than the halogen fluorides.

The Structures of the Interhalogen Compounds. There is now good evidence that some of the interhalogen compounds are in some measure ionic. Thus fused iodine mono- and trichlorides have specific conductivities in the molten state of the order of $10^{-3}\text{ohm}^{-1}\text{cm.}^{-1}$, and also give conducting solutions in various organic solvents. The ionization is believed to occur in accordance with the equations



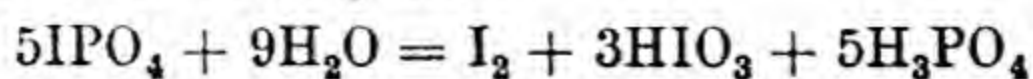
Bromine trifluoride and iodine pentafluoride ionize similarly ($2\text{BrF}_3 \rightleftharpoons \text{BrF}_2^+ + \text{BrF}_4^-$; $2\text{IF}_5 \rightleftharpoons \text{IF}_4^+ + \text{IF}_6^-$). This ionization is certainly not complete in the liquid state and for most purposes the interhalogen compounds may be considered as being covalent, with one multivalent halogen in the molecule. From Raman and infra-red measurements it has been concluded that

iodine pentafluoride forms a tetragonal pyramid and iodine heptafluoride a pentagonal bipyramid. The molecule of chlorine trifluoride is probably planar. There is some evidence that the liquid is associated. The relationship between the interhalogen compounds and the polyhalides is also of interest. The latter all form ionic crystals, containing anions such as I_3^- , IBr_2^- , IBrCl^- and ICl_2^- . Their formation is limited to metals with large cations, *i.e.* to the alkali metals and ammonium and substituted ammonium ions, and the polyhalides of the alkali metals increase in stability with increase in ion size. The general method of preparation is by the addition of a halogen or interhalogen compound to the metal halide (*e.g.* $\text{KI} \rightarrow \text{KI}_3$; $\text{KCl} + \text{ICl}_3 \rightarrow \text{KICl}_4$; $\text{CsF} + \text{ICl}_3 \rightarrow \text{CsICl}_3\text{F}$). The anhydrous acids from which these polyhalides are derived cannot be prepared, but the compound $\text{HICl}_4 \cdot 4\text{H}_2\text{O}$ is formed on passing chlorine through a suspension of iodine in concentrated hydrochloric acid. The structures of these ions are very incompletely known, but in the case of $(\text{ICl}_4)^-$ and $(\text{ICl}_2)^-$ it is believed that the valency shells of the iodine contain twelve and ten electrons, respectively. The $(\text{ICl}_4)^-$ ion then forms an octohedron, with unshared electron pairs occupying two *trans* positions. Similarly $(\text{ICl}_2)^-$ forms a trigonal bipyramid with the three equatorial positions occupied by unshared electron pairs.

Basic Properties of Iodine.

Reference has been made in Chapter XI to the basic properties of iodine when it was pointed out that the oxide I_2O_4 is probably a basic iodate, $\text{O}=\text{I}-\text{IO}_3$. Similarly the oxide I_4O_9 may be written as iodine iodate $\text{I}(\text{IO}_3)_3$. The tendency of iodine to form a cation is also evident in the interhalogen compounds, in several iodine salts and in a number of organic derivatives.

Iodine forms an acetate, $\text{I}(\text{CH}_3\text{CO}_2)_3$ and a phosphate, IPO_4 . The former is obtained by oxidizing a solution of iodine in acetic anhydride with fuming nitric acid and distilling off the excess of solvent and acid in vacuum at $40-50^\circ$. Electrolysis of a solution of the acetate in acetic anhydride with a silvered platinum gauze cathode gave a deposit of silver iodide on the latter in an amount which accorded with Faraday's Laws. There seems little doubt, therefore, that iodine in this case functions as a trivalent cation. Chlorinated acetic acids similarly give the compounds $\text{I}(\text{CH}_2\text{ClCO}_2)_3$, $\text{I}(\text{CHCl}_2\text{CO}_2)_3$ and $\text{I}(\text{CCl}_3\text{CO}_2)_3$. The crystalline phosphate IPO_4 is obtained by using a mixture of iodine, phosphoric acid, acetic anhydride and fuming nitric acid. It is very readily hydrolysed in accordance with the equation



The hydrated perchlorate $\text{IClO}_4 \cdot 2\text{H}_2\text{O}$ is made by dissolving iodine in anhydrous perchloric acid and oxidizing with ozone.

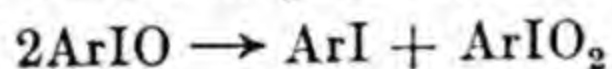
The stability of univalent iodine salts is increased by coordination with pyridine and other organic bases.⁴³ Thus a perchlorate $[\text{I}(\text{pyr})_2]\text{ClO}_4$ has been prepared by the action of iodine on $[\text{Ag}(\text{pyr})_2]\text{ClO}_4$ dissolved in chloroform. A number of similar compounds have also been obtained, notably

$[\text{I}(\text{pyr})_2]\text{X}$, where $\text{X} = \text{nitrate}$.

$[\text{I pyr}] \text{X}$, where $\text{X} = \text{nitrate, acetate, benzoate}$.

Compounds of the same type are also known in which pyridine is replaced by other bases, such as picoline. In the electrolysis of these compounds it is stated that iodine migrates to the cathode. Comparable salts are also formed by bromine, among these being the compounds $[\text{Br}(\text{pyr})_2]\text{NO}_3$ and $[\text{Br}(\text{pyr})_2]\text{ClO}_4$.

The organic derivatives in which iodine may be regarded as basic, or at least polyvalent, are rather numerous.⁴⁴ They contain one or two organic radicals attached to iodine and include iodide-chlorides and also iodoso, iodoxy and iodonium compounds. A typical member of the first of these groups is $\text{C}_6\text{H}_5\text{ICl}_2$, made by the reaction of chlorine on iodobenzene. The corresponding fluorides RIF_2 are also known. On treatment with alkali the dichloride gives the iodoso compound, $\text{Ar}-\text{I}=\text{O}$, which disproportionates on heating to the iodide and the pentavalent iodoxy compound.



The (IO) group appears in basic iodine sulphate, formed by dissolving iodine and iodine pentoxide in concentrated sulphuric acid.

The iodonium compounds are salts of the cation $(\text{Ar}_2\text{I})^+$, in which the iodine atom has a complete electron octet. Many are soluble in water and give conducting solutions. Complex salts such as $[\text{Ar}_2\text{I}]_2\text{PtCl}_6$, $[\text{Ar}_2\text{I}]_2\text{HgCl}_4$ and $[\text{Ar}_2\text{I}]\text{AuCl}_4$ are known, and free bases of the type Ar_2IOH are strongly alkaline.

The Pseudo-Halogens.

The term 'pseudo-halogen' was applied by Birckenbach and Kellermann⁴⁵ to certain univalent negative inorganic radicals which show a resemblance to the halogens in their physical and chemical properties. The principal radicals coming within this category are the cyanide, thiocyanate, azidodithiocarbonate, selenocyanate, tellurocyanate, cyanate, and azide radicals. The first

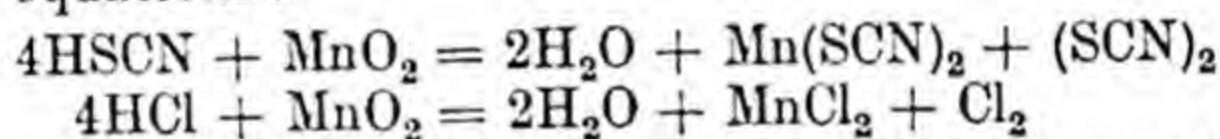
⁴³ Carlsohn, *Ber.*, 1935, 68, 2209.

⁴⁴ See Sidgwick, *The Chemical Elements and their Compounds* (Oxford University Press, 1950), Vol. II, p. 1245.

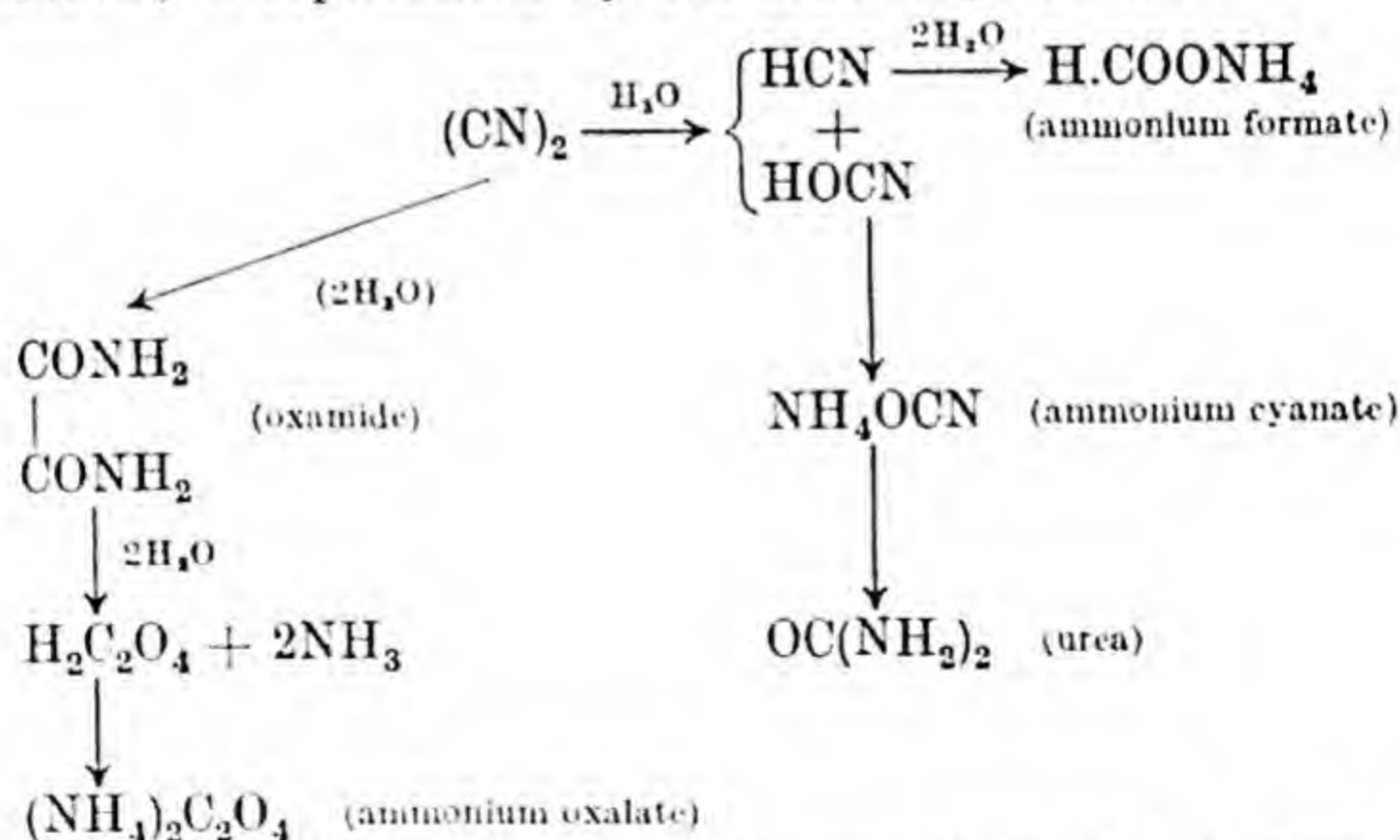
⁴⁵ *Ber.*, 1925, 58, 786, 2377.

four have actually been isolated in their dimeric forms, although all are known in the form of numerous derivatives.⁴⁶

The chemistry of the pseudo-halogens is not, for the most part, of recent date. Cyanogen, for example, was prepared in 1815 by Gay-Lussac by the action of heat on mercuric or silver cyanide, and throughout the nineteenth century there was a sustained interest in this and related substances. The general similarity to the halogens is evident from the combination with hydrogen to form monobasic acids, which give insoluble lead, silver and mercurous salts, while the dimeric radicals which have so far been prepared have a general similarity to the halogens in their reactions. One may instance compounds such as carbonyl azide, $\text{CO}(\text{N}_3)_2$,⁴⁷ and sulphuryl azide, $\text{SO}_2(\text{N}_3)_2$,⁴⁸ to show the close parallel between the formulæ of halogen compounds and those of the pseudo-halogens. Another interesting reaction illustrating the relationship between the pseudo-halogens and the halogens is that between thiocyanic acid and manganese dioxide, which has been shown to give small yields of thiocyanogen. This reaction, and the reaction between manganese dioxide and hydrogen chloride, are represented by the following equations:



Cyanogen $(\text{CN})_2$.—This is the most readily accessible of the pseudo-halogens, its general reactions being so well known as to need no detailed mention here. It forms a liquid which boils at -25° . The hydrolysis, which is among the most interesting of its reactions, is represented by the following scheme:

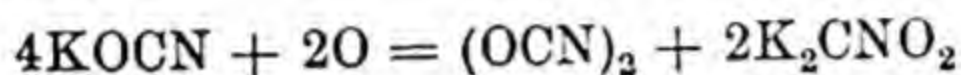


⁴⁶ See Walden and Audrieth, *Chem. Reviews*, 1928, 5, 339, from which source much of the material in this section is taken.

⁴⁷ Curtius and Heidenreich, *Ber.*, 1894, 27, 2684.

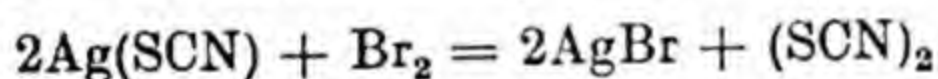
⁴⁸ Curtius and Schmidt, *ibid.*, 1922, 55, 1571.

Oxycyanogen $(\text{CNO})_2$.—Birckenbach and Kellermann⁴⁹ were unsuccessful in the isolation of oxycyanogen by the electrolysis of a solution of potassium cyanate in methyl alcohol, but the anode solution after electrolysis liberated iodine from potassium iodide and was capable of dissolving copper, zinc and iron without gas evolution. The free oxycyanogen also underwent a secondary reaction with the methyl alcohol used as solvent. In earlier work Lidov⁵⁰ described oxycyanogen as a gas which was similar to carbon dioxide. He claimed to have prepared it by the following three methods: (a) interaction of cyanogen bromide and silver oxide, (b) reduction of nitrogen dioxide with carbon at 150° , and (c) by the action of hydrogen peroxide, cupric oxide or sodium hypobromite on potassium cyanate.



This work has not, however, been repeated, and it does not seem probable that oxycyanogen would be a gaseous substance of this sort.

Thiocyanogen $(\text{SCN})_2$.—This substance was first prepared by Söderbäck⁵¹ by the action of iodine, or, better, of bromine, on an ethereal suspension of silver thiocyanate.



The resulting solution of thiocyanogen is able to liberate iodine from iodides, will oxidize copper from the cuprous to the cupric state, and reacts directly with metals to form thiocyanates. Solid thiocyanogen is obtained by evaporating the ether solution and cooling to -70° . It melts at -2° to -3° to a yellow oil and polymerizes irreversibly at room temperature to an insoluble brick-red amorphous solid. Thiocyanogen has also been prepared by electrolysis of thiocyanates, preferably dissolved in methyl alcohol.⁵² The anode liquid obtained in the electrolysis of alcoholic potassium or ammonium thiocyanate gave impure thiocyanogen on evaporating off the alcohol. There was a tendency for polymerization to occur in such solutions. Thiocyanogen is decomposed by water, with formation of thiocyanic acid and hydrocyanic acid.

Among the other reactions of thiocyanogen which suggest a close parallel to the halogens is the formation of an unstable nitrosyl thiocyanate $\text{NO}(\text{SCN})$ by the action of ethyl nitrite on thiocyanic acid, and the direct addition of thiocyanogen to unsaturated

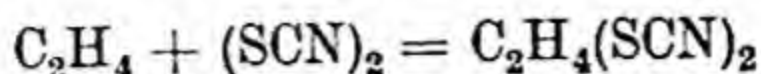
⁴⁹ *Ber.*, 1925, 58, 786.

⁵⁰ *Chem. Abs.*, 1912, 6, 2368, 2369, 3093, 3094.

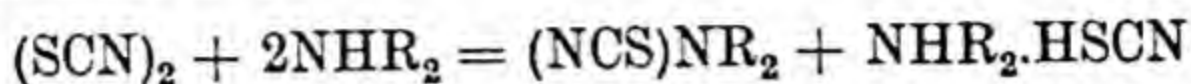
⁵¹ *Annalen*, 1919, 419, 217.

⁵² Kerstein and Hoffmann, *Ber.*, 1924, 57, 491.

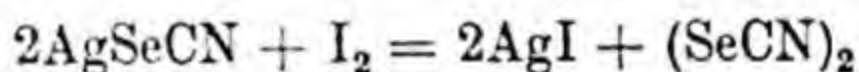
hydrocarbons.⁵³ Thus with ethylene the reaction taking place is



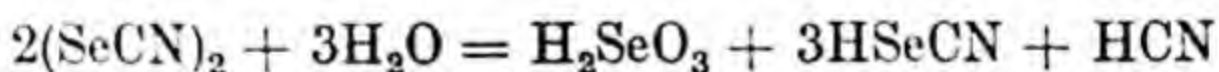
Thiocyanogen reacts with ammonia to form the unstable compound SCN.NH_2 ,⁵⁴ while, with amines, derivatives corresponding to the chloroamines result:



Selenocyanogen $(\text{SeCN})_2$.—This has been prepared by electrolyzing a solution of potassium selenocyanate in methyl alcohol (Birckenbach and Kellermann⁵⁵), or by decomposing lead tetraselenocyanate.⁵⁶ The electrolytic method is unsuitable for preparing the pure compound, however, as selenium is deposited very readily, and it is necessary to turn to a method depending on the decomposition of the silver salt of selenocyanic acid, suspended in ether, with iodine. The reaction between these two substances results in an equilibrium in which only 80 per cent of the iodine is present as silver iodide. Excess of silver selenocyanate is therefore used, and the temperature must be kept below 10° to avoid decomposition.



Selenocyanogen is a yellow crystalline powder which is stable when dry and which is soluble in benzene, chloroform, or carbon tetrachloride. Determinations of the molecular weight in benzene solution showed that the compound had the dimeric formula $(\text{SeCN})_2$. Hydrolysis of selenocyanogen occurs readily and is believed to be represented by the following equation:



On heating a solution of selenocyanogen in carbon disulphide under reflux polymerization occurs, and the crystalline compound $\text{Se}_3(\text{CN})_2$ separates on cooling.

Tellurocyanogen, $(\text{TeCN})_2$, has not so far been prepared, although Walden and Audrieth⁵⁷ suggest that it should be capable of isolation either by electrolysis of a solution of its potassium salt in methyl alcohol, or by the reaction between potassium tellurocyanate and lead tetracetate dissolved in acetone.

The following comparison of halogen salts of tetravalent lead

⁵³ Kaufmann, *Ber. deutsch. pharm. Ges.*, 1923, 33, 139.

⁵⁴ Lecher, Witter and Speer, *Ber.*, 1923, 56, 1104.

⁵⁵ *Ibid.*, 1925, 58, 786, 2377.

⁵⁶ Kaufmann and Kögler, *ibid.*, 1926, 59, 178.

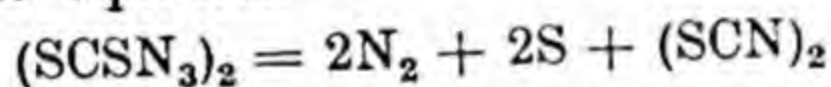
⁵⁷ *Loc. cit.*, Ref. 46.

with certain of the corresponding pseudo-halogen derivatives illustrates the remarkable similarity between the two groups.

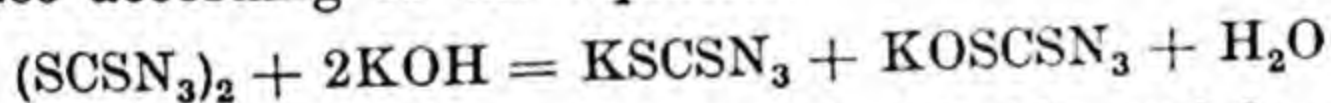
PbF ₄	Solid : loses fluorine at high temp.
Pb(OCN) ₄	Syrupy liquid. Stable for short time at room temp.
PbCl ₄	Oil. m.p. — 15°. Decomp. very readily.
PbBr ₄	Decomp. immediately at room temp. into PbBr ₂ and Br ₂ .
Pb(SCN) ₄	" " " " " Pb(SCN) ₂ and (SCN) ₂ .
PbI ₄	" " " " " PbI ₂ and I ₂ .
Pb(SeCN) ₄	" " " " " Pb(SeCN) ₂ and (SeCN) ₂ .

Azidocarbondisulphide (SCSN₃)₂.—Azidocarbondisulphide is a very unstable white crystalline solid which was first examined in detail by Browne, Hoel, Smith and Swezey.⁵⁸ Its potassium salt, KSCSN₃, is formed by the interaction of a solution of potassium azide and carbon disulphide at 40°. The free pseudo-halogen is then isolated by treating a solution of the potassium salt with oxidizing agents such as ferric chloride or hydrogen peroxide.

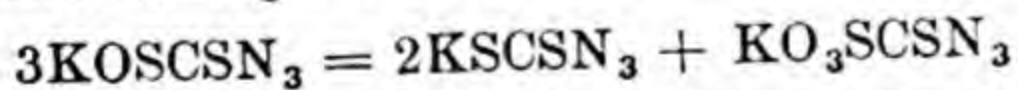
Azidocarbondisulphide is soluble in water to the extent of 3 parts in 10,000 at 25°. It is very unstable, and is liable to explode violently on impact. It decomposes spontaneously at room temperature, the course of the reaction being represented in all probability by the equation



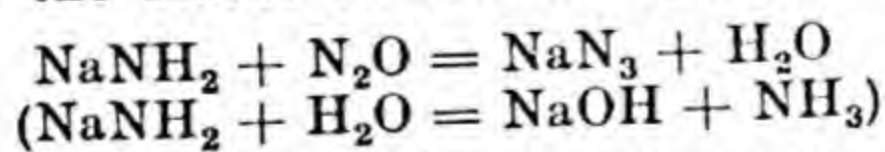
The reaction with dilute aqueous alkalis at — 10° is believed to take place according to the equation



This is analogous to the formation of chloride and hypochlorite from chlorine and cold alkalis. There is also evidence that the oxygen compound formed tends to decompose with formation of a new compound analogous to a chlorate. Thus :



The Azides.—The azide radical is unknown in the free state or as a dimer. In a number of its derivatives, however, it resembles its halogen and pseudo-halogen analogues. The hydrogen compound, hydrazoic acid, is obtained as its sodium salt by the action of nitrous oxide on sodium amide at 190°. The water liberated converts some of the amide to sodium hydroxide.



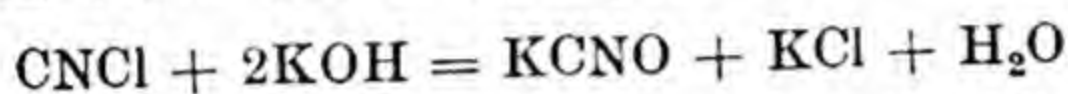
Free hydrazoic acid is obtained by distilling the sodium salt with 1 : 1 sulphuric and dehydrating the distillate with calcium chloride.

⁵⁸ *J. Amer. Chem. Soc.*, 1923, 45, 2541.

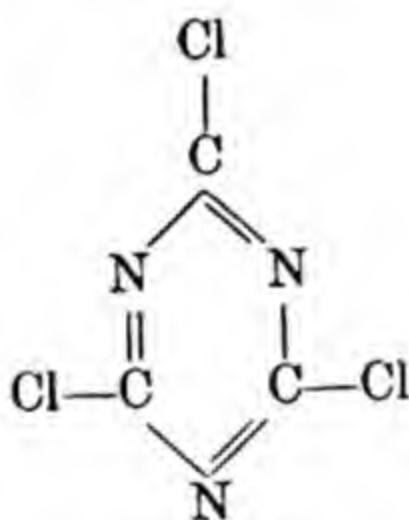
cyanogen halides, and the monochloride and trichlorides of thiocyanogen. These compounds have formulæ which are analogous to those of the simpler interhalogen compounds, although, as might be expected, the more complex interhalogen compounds containing fluorine (*e.g.* IF_5 and IF_7) have no counterpart.

Chloroazide, ClN_3 ,⁶¹ bromoazide, BrN_3 ,⁶² and iodoazide, IN_3 ,⁶³ are all extremely explosive substances. The cyanogen halides are well-known compounds. Cyanogen chloride is a low-boiling liquid which is formed by the action of chlorine on hydrocyanic acid or a cyanide. The bromide, which is a solid, is formed in a similar way. The iodide is also a solid and is obtained by the action of a solution of iodine in ether on mercuric cyanide.

The reaction of cyanogen chloride with alkalis follows the equation given below and is analogous to that of the halogens.

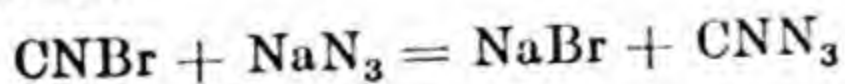


The halides polymerize on standing, forming $(\text{CNCl})_3$, $(\text{CNBr})_3$ and $(\text{CNI})_3$. The first of these, cyanuric chloride, is believed to have the cyclic formula shown below:



Thiocyanogen chloride, SCNCl , is a white crystalline substance and is formed by the combination of thiocyanogen and chlorine in chloroform. Browne and Gardner⁶⁴ have also obtained evidence for the formation of the compounds $\text{Cl}(\text{SCSN}_3)$, $\text{Br}(\text{SCSN}_3)$ and $\text{Br}_2(\text{SCSN}_3)$ by the action of halogens on azidocarbonyldisulphide.

Certain compounds formed by the pseudo-halogens among themselves are also well established. Thus cyanogen bromide reacts with a well-cooled aqueous solution of sodium azide to form cyanogen azide, which can be isolated as a crystalline solid by extracting with ether.



Cyanogen thiocyanate, $\text{CN}(\text{SCN})$, and cyanogen selenocyanate,

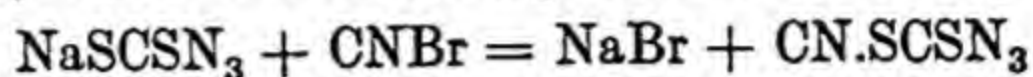
⁶¹ Raschig, *Ber.*, 1908, 41, 4194.

⁶³ Hantzsch, *Ber.*, 1900, 33, 522.

⁶² Spencer, *J.C.S.*, 1925, 127, 216.

⁶⁴ *J. Amer. Chem. Soc.*, 1927, 49, 2759.

CN(SeCN), have also been prepared, and are both well-defined crystalline substances. Cyanogen azidodithiocarbonate has also been isolated recently.⁶⁵ It is formed in good yield by adding cyanogen bromide to a cold aqueous solution of sodium azidodithiocarbonate, when the following reaction takes place:



This substance is a white crystalline solid, which undergoes slow decomposition at room temperature, and which is liable to explode when it is heated.

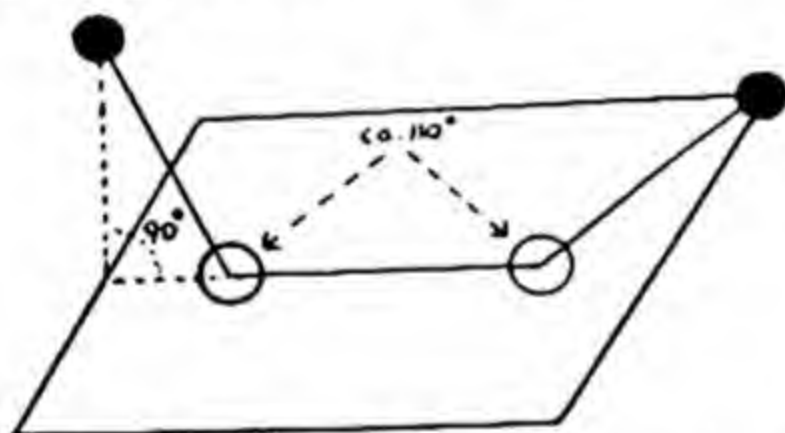
⁶⁵ Audrieth and Browne, *ibid.*, 1930, 52, 2799.

CHAPTER XII

THE PEROXIDES AND PER-ACIDS

Both the metallic peroxides and the per-acids are best considered as derivatives of hydrogen peroxide, which is a weak acid. In the pure state hydrogen peroxide, an oily liquid which freezes at -1.7° , has an ionization constant $[(\text{H}^+)(\text{HO}_2^-)]$ of 1.55×10^{-12} at 20° , which implies a hydrogen ion concentration roughly 12 times that in pure water. In other respects, apart of course from its endothermic character and instability, it resembles water closely. The dielectric constant is 89.2 at 0° , compared with 84.4 for water at the same temperature.

The structure of the hydrogen peroxide is of special importance in relation to the per-compounds. The most probable configuration,



which was suggested by Penney and Sutherland,¹ is one in which there is no free rotation about the $-\text{O}-\text{O}-$ bond in $\text{H}-\text{O}-\text{O}-\text{H}$ molecule, the hydrogen atoms being situated in planes which are at right angles. This configuration is consistent with the Raman spectra of H_2O_2 , DHO_2 and D_2O_2 .² It is also in agreement with observations on the crystal structure of the compound $\text{CO}(\text{NH}_2)_2 \cdot \text{H}_2\text{O}_2$,³ in which the urea molecule has its normal configuration, and the $-\text{O}-\text{O}-\text{H}$ angle is 106° . The distance between the two oxygen atoms is 1.46 \AA .^{3a}

In the discussion of the metallic peroxides and the per-acids which follows, the structural relationship to hydrogen peroxide will be apparent. The peroxides contain peroxide ions (either O_2^- or

¹ *Trans. Faraday Soc.*, 1934, 30, 898. *J. Chem. Phys.*, 1934, 2, 492.

² Feher, *Ber.*, 1939, 72, 1778.

³ Lu, Hughes and Giguere, *J. Amer. Chem. Soc.*, 1941, 63, 1507.

^{3a} A recent determination of the crystal structure of H_2O_2 confirms this configuration (Abrahams, Collin and Lipscomb, *Acta Cryst.*, 1951, 4, 15).

O_2^{2-}) in the solid state and in the per-acids one or both of the hydrogen atoms of the parent substance are replaced by acidic groups. A number of peroxy compounds formed by the weakly electropositive metals will be mentioned which are, in a sense, intermediate in their properties between these two main types.

Peroxides.

The best-known metallic peroxides are those of the alkali and alkaline earth metals, but copper, silver, magnesium, zinc, cadmium and mercury also form compounds which are in this class. There are four main types:

- (i) Compounds formed by replacement of both of the hydrogen atoms of hydrogen peroxide, giving $\text{M}^{\text{I}}_2\text{O}_2$ or $\text{M}^{\text{II}}\text{O}_2$. These are ionic solids and contain the ion O_2^{2-} (e.g. Na_2O_2 , BaO_2).
- (ii) Compounds of the type $\text{M}^{\text{I}}\text{O}_2$, formed by the strongly electropositive elements of large ionic radius, and containing the ion O_2^- (e.g. KO_2).
- (iii) Compounds of the type $\text{M}^{\text{I}}_2\text{O}_3$, formed by potassium, rubidium and caesium. There is some doubt as to the identity of these.
- (iv) Hydroperoxides of the type $\text{M}^{\text{I}}-\text{O}-\text{O}-\text{H}$, in which only one hydrogen atom of hydrogen peroxide is replaced (e.g. NaO_2H).

The formulæ of the true peroxides known at present are shown below. These are not based in every case on structural analysis, but all give hydrogen peroxide when treated with acids. It is important to note that in the true peroxides the metal atoms have their normal valencies. The term peroxide is sometimes applied to compounds such as PbO_2 and MnO_2 , the oxidizing properties of which are due to the high valency of the metal. They contain the normal O^{2-} ion in their structures, and do not give hydrogen peroxide with acids.

Li_2O_2						
Na_2O_2		NaO_2			$\text{MgO}_2 \cdot x\text{H}_2\text{O}$	
K_2O_2	K_2O_3	KO_2	CaO_2	CaO_4	ZnO_2	
Rb_2O_2	Rb_2O_3	RbO_2	SrO_2	SrO_4	CdO_2	CuO_2
Cs_2O_2	Cs_2O_3	CsO_2	BaO_2	BaO_4	Hg_2O_2	Ag_2O_2
$(\text{NH}_4)_2\text{O}_2$					HgO_2	

The stability of the metallic peroxides becomes less as the electropositive nature of the metal decreases (e.g. in passing from the alkali metals to copper and mercury), but is also partly dependent on the ion sizes. Thus, for example, the stability of the alkaline earth metal peroxides increases from calcium to barium with increasing size of the cation.

Three general preparative methods are available, viz.:

- (i) Heating the metals in air or oxygen.
- (ii) The action of oxygen on solutions of the metals in liquid ammonia.
- (iii) The action of hydrogen peroxide on metallic hydroxides or metallic salts. This may also give rise to hydroperoxides (MO_2H).

The Alkali Metal Peroxides.

The end-products of the combustion of the free alkali metals in an excess of oxygen are Li_2O , Na_2O_2 , KO_2 , RbO_2 and CsO_2 , the proportion of oxygen in the most stable oxide thus increasing with the atomic weight and—more significantly—the ionic radius of the metal. The monoxide of sodium (Na_2O) and those of the heavier elements of the group are formed only if a deficit of oxygen is used. There is a progressive deepening of colour from Li_2O_2 (white) through KO_2 (orange-red) to CsO_2 (dark brown). In the case of potassium, rubidium and caesium the stability of the peroxides is such that they may be formed directly by the action of oxygen on the metallic hydroxide.⁴ Potassium hydroxide gave a 70 per cent yield of KO_2 at $375^\circ/100$ atm., whilst caesium hydroxide gave a 95 per cent yield of CsO_2 under similar conditions. The oxide Na_2O_2 is also converted to NaO_2 when heated in oxygen at 500° and 300 atmospheres pressure.⁵

Compounds of the type $\text{M}^{\text{I}}_2\text{O}_2$.—Except in the case of lithium, alkali metal peroxides of this type may be made by the controlled oxidation of the metal or its monoxide, or by oxidation of the metal dissolved in liquid ammonia. Lithium peroxide, Li_2O_2 , is made by the thermal decomposition of the compound $\text{Li}_2\text{O}_2 \cdot \text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$, which is produced in the reaction between lithium hydroxide and alcoholic hydrogen peroxide.

Sodium peroxide, Na_2O_2 , is made technically by oxidizing the metal in two stages in rotary ovens, the first stage giving mainly the monoxide and the second, in which a higher temperature is employed, the peroxide. By the action of concentrated mineral acids on sodium peroxide in alcoholic solution, the hydroperoxide NaO_2H is formed, which readily gives the addition compound $\text{NaO}_2\text{H} \cdot 0.5\text{H}_2\text{O}_2$ with hydrogen peroxide. The hydroperoxide is

⁴ Fischer and Ploetzer, *Z. anorg. Chem.*, 1925, 75, 1.

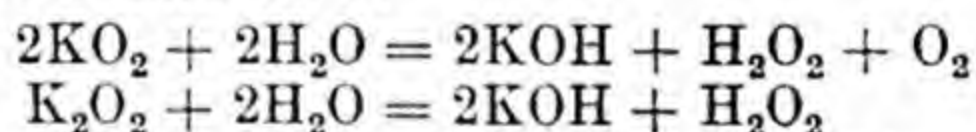
⁵ Stephanon, Schechter, Argersinger and Kleinberg, *J. Amer. Chem. Soc.*, 1949, 71, 1819. Reaction of the alkali metal hydroxides with ozone gives paramagnetic compounds of the type MO_3 (Whaley and Kleinberg, *ibid.*, 1951, 73, 79). Zhdanov and Zvonkova (*Zhur. Fiz. Khim.*, 1951, 25, 100) suggest, from an X-ray study, that KO_3 contains the O_3^- ion, which resembles N_3^- .

much less stable than is sodium peroxide and decomposes slowly at room temperature.

Potassium peroxide, K_2O_2 , is formed in the controlled oxidation of potassium metal—*e.g.* with the calculated amount of air at 300° , or in liquid ammonia solution at -50° . The peroxides of rubidium and caesium are produced similarly. The structures of these compounds have not been determined by X-ray methods. They are presumed to contain the ion O_2^{2-} which has been identified in the alkaline earth metal peroxides and this view is supported by the formation of hydrogen peroxide on hydrolysis.

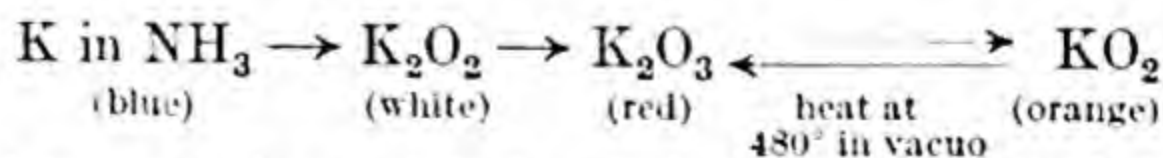
Compounds of the type MO_2 .—The formation of NaO_2 has been mentioned already. The corresponding peroxides of potassium, rubidium and caesium are produced more readily, KO_2 , for example, being obtained when potassium is burned in an excess of oxygen or when it is fused with potassium nitrate. It is also formed in the oxidation of the lower oxides by oxygen at high temperatures, or by the prolonged action of oxygen on a solution of potassium in liquid ammonia. These oxides are referred to as superoxides.

The action of water on potassium superoxide differs from that on potassium peroxide in that both oxygen and hydrogen peroxide are formed in the first case:



It is now clear that the formulæ of the superoxides are of the type $M^I O_2$, and not $M^I_2 O_4$. The solids are isomorphous with calcium carbide,⁶ the anions in their lattices being O_2^{--} and C_2^{--} , respectively. Furthermore the superoxides are paramagnetic, which would be expected on the single formula, which results in an odd number of electrons (K, 19; O_2 , 16), but not for a molecule of the type M_2O_4 .

Compounds of the type M_2O_3 .—Substances of this type may be formed as intermediates in the oxidation of ammonia solutions of the alkali metals. In the oxidation of potassium, for example, there is a distinct colour change corresponding to the formation of K_2O_3 .



The product may be formulated as a lattice compound $2KO_2 \cdot K_2O_3$, but it behaves chemically as if it were a mixture of the two oxides.⁷

⁶ Templeton and Dauben, *J. Amer. Chem. Soc.*, 1950, **72**, 2251. Helms and Klemm, *Z. anorg. Chem.*, 1939, **241**, 97. Kassatochkin and Kotow, *J. Chem. Phys.*, 1936, **4**, 458.

⁷ Kraus and White, *J. Amer. Chem. Soc.*, 1926, **48**, 1786. Helms and Klemm, *Z. anorg. Chem.*, 1939, **241**, 97.

The crucial test of whether a definite compound exists would be the X-ray determination of the structure of the solid, but this has not yet been done.

Alkaline Earth Peroxides.—The peroxides of the alkaline earths are CaO_2 , SrO_2 and BaO_2 , their stability increasing in this order. Barium peroxide is formed when air or oxygen is passed over the monoxide at about 400° . Above 500° it has an appreciable dissociation pressure, and the reversible equilibrium between the two oxides was formerly applied in the Brin process for obtaining oxygen from the air. Strontium peroxide is formed less readily on heating the monoxide in air or oxygen, only 15–16 per cent being produced at 400° with oxygen at 100 atm. pressure. Both BaO_2 and SrO_2 are, however, formed by the action of oxygen on solutions of the metals in liquid ammonia, and a poor yield of CaO_2 may also be obtained by this method, though the peroxide is not formed from CaO and O_2 . All three alkaline earth metals are precipitated by hydrogen peroxide or sodium peroxide from solutions of their salts or hydroxides as octahydrates of the peroxides (e.g. $\text{CaO}_2 \cdot 8\text{H}_2\text{O}$), dehydration of which gives the anhydrous compound. The calcium compound is used as a bleaching agent and as an antiseptic.

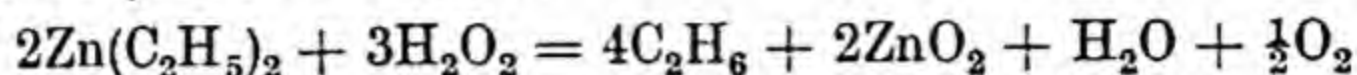
Barium peroxide (and presumably also CaO_2 and SrO_2) has a structure of the calcium carbide type and contains the anion O_2^{--} . There is thus a structural similarity to KO_2 , which is not surprising since the ionic radii of potassium and barium are similar (Ba^{++} , 1.35 Å.; K^+ , 1.33 Å.), and the interatomic distances in the O_2^{--} and O_2^{--} ions are 1.28 and 1.31 Å., respectively. The ionic radii of calcium (0.99 Å.) and strontium (1.13 Å.) are sufficiently different from those of barium and potassium to explain qualitatively the lower stability of their peroxides, which manifests itself in the higher dissociation pressure.

Barium peroxide forms the addition compound $\text{BaO}_2 \cdot \text{H}_2\text{O}_2$ with hydrogen peroxide. This deepens in colour on keeping, especially on exposure to ultra-violet light, and evolves oxygen when treated with water. It has been suggested that the compound BaO_4 , containing the ion O_4^{--} , is formed under these conditions, but there is no direct structural evidence. The oxide CaO_4 is said to be formed similarly.

Other Metallic Peroxides.—Whereas the alkalis and alkaline earths form well-defined peroxides, certain of the less electropositive metals yield peroxy compounds of somewhat uncertain constitution. Thus when solutions of magnesium salts are treated with sodium peroxide, variable mixtures of magnesium hydroxide with magnesium peroxide hydrate are produced. Hydrogen peroxide in alkaline solution precipitates from magnesium sulphate solution a peroxide of the

composition $\text{MgO} \cdot \text{MgO}_2 \cdot x\text{H}_2\text{O}$. Nothing is known of the structures of these compounds. They readily yield hydrogen peroxide, and certain of them are prepared commercially for medicinal purposes.

Similar ill-defined compounds are formed by zinc and cadmium. Zinc peroxide, containing about 86 per cent of ZnO_2 , was obtained by Ebler and Krause⁸ by the action of ethereal hydrogen peroxide on zinc ethyl or zinc amide:



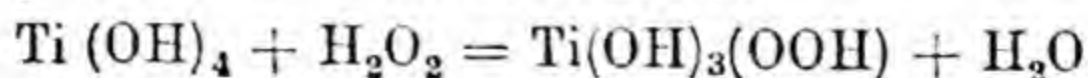
The reaction is also applicable to the preparation of peroxides of magnesium and cadmium. Zinc and cadmium also form compounds containing peroxidic oxygen when their hydroxides are treated with hydrogen peroxide. A peroxide of mercury, HgO_2 , has been described as formed by the action of 30 per cent H_2O_2 on mercury, mercuric oxide or on alcoholic solutions of mercuric chloride. It is unstable, evolving oxygen when treated with water and exploding when struck or rapidly heated.

There is no clear evidence that silver forms a peroxide. The compound with the empirical formula AgO , which is obtained by the action of ozone on silver, by the anodic oxidation of silver, or by the action of potassium persulphate on silver nitrate solution, may be argentic oxide or argentous peroxide. A peroxide of argentous silver, containing the ion O_2^{--} , would be diamagnetic and Klemm found AgO to be weakly paramagnetic.⁹ Sugden,¹⁰ however, examined similar preparations which proved to be diamagnetic. It is possible that both a peroxide of the lower valency state of silver and argentic oxide exist, but the point needs further elucidation.

Peroxy Compounds of Certain Transition Elements.

The weakly electropositive metals of the titanium, vanadium and chromium groups give rise to numerous peroxy compounds which illustrate the transition between the peroxides proper and the true peracids.

Titanium, zirconium, hafnium and cerium all form compounds of the general formula $\text{MO}_3 \cdot 2\text{H}_2\text{O}$ when ammoniacal hydrogen peroxide is added to a solution of a titanyl, zirconyl, hafnyl or ceric salt. The stability increases with the atomic weight of the metal. These compounds, according to Schwarz and Giese,¹¹ contain one peroxy group in the molecule and, taking the titanium compound as an example, may be formulated as follows:



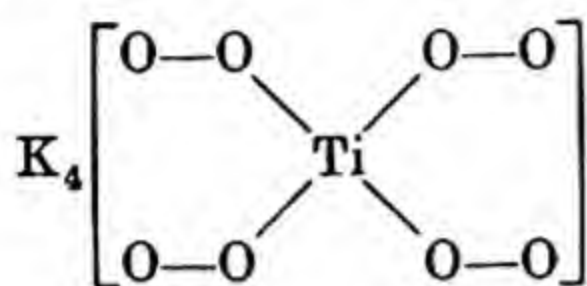
⁸ *Z. anorg. Chem.*, 1911, 71, 150.

⁹ *Ibid.*, 1931, 201, 32.

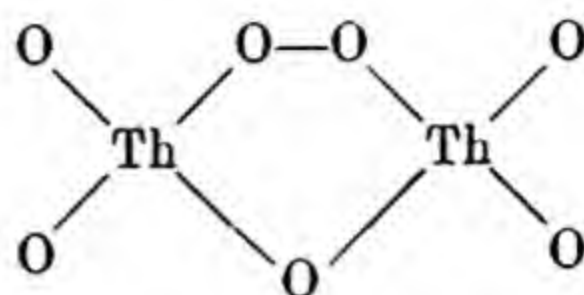
¹⁰ *J.C.S.*, 1932, 161.

¹¹ *Z. anorg. Chem.*, 1928, 176, 209.

This titanium peroxyhydrate dissolves in potassium hydroxide in presence of hydrogen peroxide, and the pertitanate $K_4TiO_8 \cdot 6H_2O$ can be isolated from the solution. This is regarded as a salt of the hypothetical orthoperoxy acid (I). The zirconium compound behaves in the same way, but the more electropositive hafnium and cerium do not.



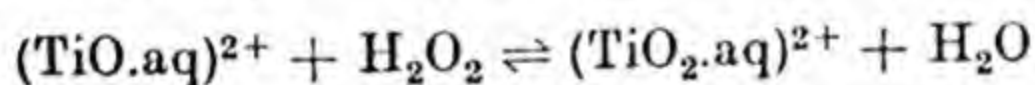
(I)



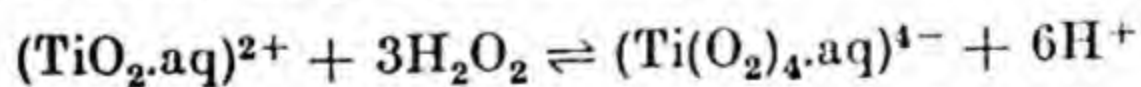
(II)

Thorium salts in solution give, on the addition of hydrogen peroxide, a precipitate of the composition $Th_2O_7 \cdot 4H_2O$ which, from the proportion of peroxidic oxygen, has been assigned the structure (II). This, however, takes no count of the water which is always present in the molecule, and it is possible that $-OH$ and $-O-O-H$ groups are present.

The above reactions occur in alkaline solution, but in acid solution different products are obtained. The yellow colour produced in acidified titanium solutions on the addition of hydrogen peroxide is familiar as an analytical test. The production of this colour is independent of the acid used and it has recently been shown by Jahr and his co-workers¹² to be due to the $(TiO_2 \cdot aq)^{2+}$ ion



From mixed solutions of K_2SO_4 , H_2SO_4 and $TiOSO_4$ with excess of hydrogen peroxide the compound $K_2SO_4 \cdot (TiO_2)SO_4 \cdot 3H_2O$ may be isolated. This was formerly believed to contain the titanium in a peroxydisulphato titanate anion $(K_2(TiO_2)(SO_4)_2)$, but it is now believed that the titanium is present as the $(TiO_2)^{2+}$ cation. The relationship between this cation and the peroxy anion which occurs in alkaline solution may then be expressed by the equation

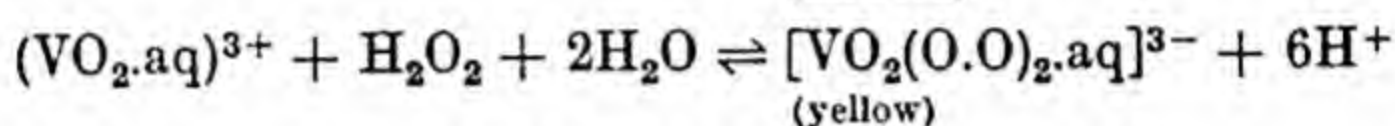
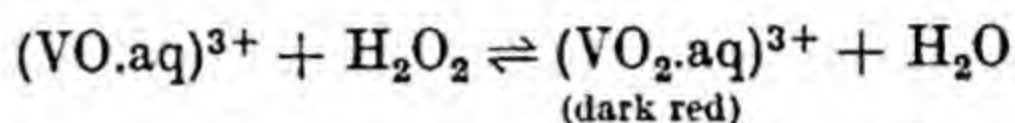


It is generally agreed that the bleaching of the yellow colour of the $(TiO_2 \cdot aq)^{2+}$ by fluoride ions is due to the formation of the stable colourless $(TiF_6)^{2-}$ ion. The behaviour of zirconyl salts with hydrogen peroxide in acid solution is similar to that of titanyl salts.

¹² FIAT Review of German Science, Inorganic Chemistry, Part III, 1948, 170.

Vanadium, niobium and tantalum show a general similarity to the Group IV transition elements in their behaviour with hydrogen peroxide. The salts Na_3NbO_8 and Na_3TaO_8 are obtained by the action of an excess of hydrogen peroxide on solutions of alkali niobates and tantalates.¹³ Similar salts of other cations are known, and they probably all contain the $\text{M}^v(\text{—O—O})_4$ anion. A few other peroxy derivatives of these two elements have been described, but their compositions are uncertain.

Acid solutions of vanadates have long been known to give a red coloration with hydrogen peroxide. It is believed that this colour is due to peroxy cations and anions similar to those which exist in the titanium solutions. Their formation may be represented by the equations¹⁴



In weakly alkaline or weakly acid vanadate solutions containing hydrogen peroxide the yellow anion is present, whilst in strongly acid solutions the red cation is formed.

Several definite pervanadates have been isolated. When, for example, potassium hydroxide is added to a solution of vanadium pentoxide in concentrated hydrogen peroxide, the salt $\text{KH}_2[\text{VO}_2(\text{O}_2)_2]\text{H}_2\text{O}$ crystallizes, and $\text{Na}_3\text{V}(\text{O}_2)_4$ may be obtained from a solution of sodium orthovanadate containing hydrogen peroxide and sodium peroxide.

The Perchromates.

The most familiar peroxy compound of chromium is associated with the intense blue colour produced when an acidified solution of a chromate is treated with hydrogen peroxide. The substance responsible for the blue colour (CrO_5) is very unstable and has not been isolated. It is, however, readily soluble in ether, with which it probably forms the unstable co-ordination compound $(\text{C}_2\text{H}_5)_2\text{O} \rightarrow \text{CrO}_5$. Addition of pyridine and other organic bases to the ether solution gives more stable crystalline co-ordination compounds, such as $\text{C}_5\text{H}_5\text{N} \rightarrow \text{CrO}_5$.

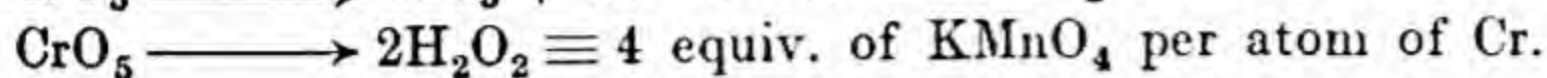
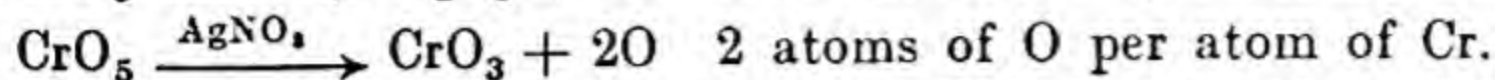
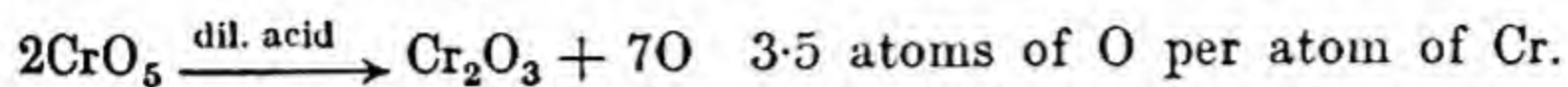
The formula and structure of CrO_5 has been fairly definitely established by experiments made on the ether solution and on the co-ordination compounds.¹⁵ It was at one time thought to be

¹³ *Z. anorg. Chem.*, 1928, 173, 297.

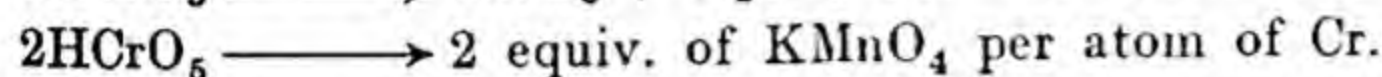
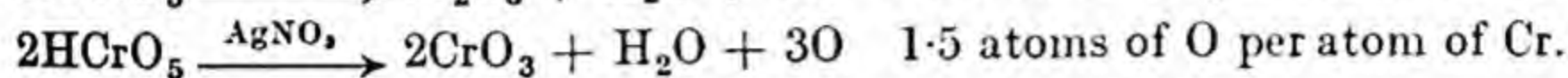
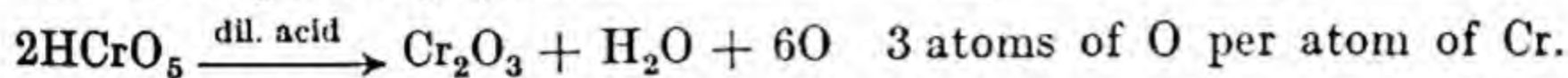
¹⁴ *Jahr.*, Ref. 12.

¹⁵ Schwarz and Giese, *Ber.*, 1932, 65, 871.

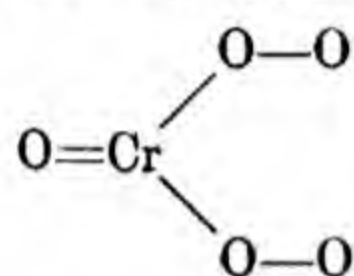
HCrO_5 , but this is excluded by the reactions with dilute acids, silver nitrate and potassium permanganate, which are :



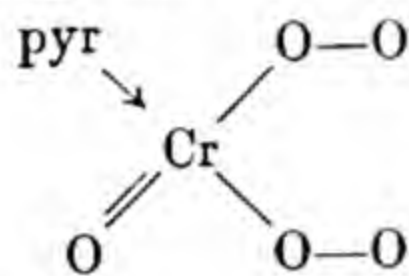
The corresponding quantities for the compound HCrO_5 would be :



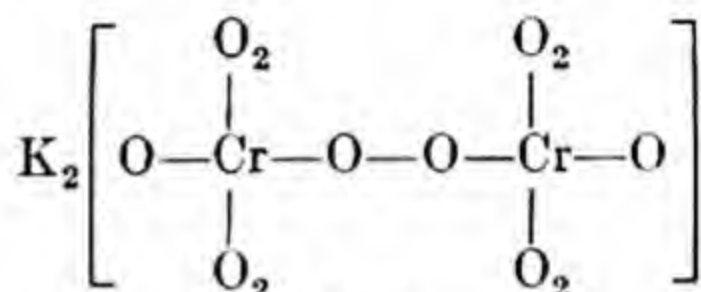
The reaction with permanganate shows that there are two O_2 groups in the molecule, and the formula may therefore be written as (I) and the pyridine compound as (II).



(I)



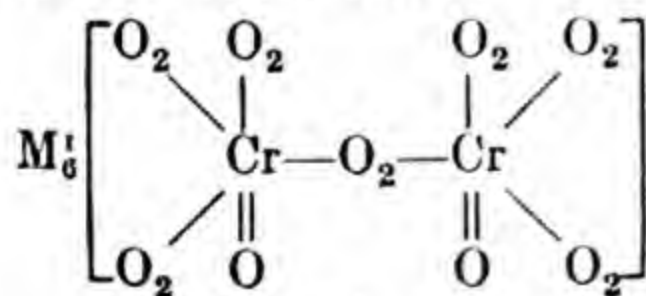
(II)



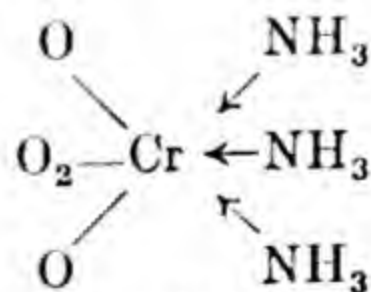
(III)

When the ether solution of CrO_5 is treated with alcoholic hydrogen peroxide containing potassium hydroxide, a blue salt of the composition $\text{KCrO}_6 \cdot \text{H}_2\text{O}$ is formed. The anhydrous thallium salt TlCrO_6 is also known. These salts contain 2.5 peroxy groups per atom of chromium. The potassium salt is diamagnetic and, since the single formula would give an odd-electron molecule which would be paramagnetic, the double formula (III) is indicated.

A further series of perchromates of the type M_2CrO_8 , which are red in colour, is obtained by the reaction of a strongly alkaline solution of hydrogen peroxide with soluble chromates. These salts contain 3.5 peroxy groups per atom of chromium and are isomorphous with the pervanadates of the type M_2VO_8 . It is possible to formulate them with the double formula (IV) as derivatives of hexavalent chromium :



(IV)



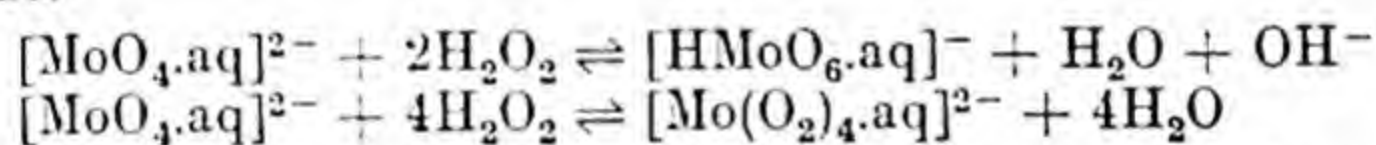
(V)

Yet another type of peroxy derivative of chromium occurs in the compound $\text{CrO}_4 \cdot 3\text{NH}_3$, which is formed when ammoniacal solutions of chromates treated with hydrogen peroxide at 0° are

warmed to 50° and then cooled. Alternatively, the red ammonium perchromate $(\text{NH}_4)_3\text{CrO}_8$ may be treated with a 10 per cent ammonia solution at 40° . This compound forms a brown solution with water which, on addition of potassium cyanide, yields the compound $\text{CrO}_4 \cdot 3\text{KCN}$. The formulation of these compounds is uncertain, but the simplest assumption is that chromium is hexavalent, as in structure (V) above, and that the cyanide is a salt of the $[\text{Cr}(\text{CN})_3\text{O}_2(\text{O}_2)]^{3-}$ anion.

Peroxy Compounds of Molybdenum, Tungsten and Uranium.

These three elements, like chromium, readily give rise to peroxy compounds, though the tendency to form isopoly acids makes the chemistry rather complicated. Solutions of normal molybdates (*e.g.* K_2MoO_4) give a deep red colour on the addition of hydrogen peroxide. This colour change is attributed¹⁶ to two reactions, the first leading to the univalent ion $(\text{HMoO}_6.\text{aq})^-$, which is yellow, and the second to the bivalent ion $[\text{Mo}(\text{O}_2)_4.\text{aq}]^{2-}$, which is red. Formation of the second of these ions occurs with excess of hydrogen peroxide.



In acid-rich molybdate solutions polymolybdates are formed and these can also give peroxy derivatives.

Salts containing these ions have been prepared. Thus from a potassium molybdate solution containing one equivalent of a mineral acid per molecule of molybdate, together with excess of hydrogen peroxide, Jahr has obtained the salt $\text{K}[\text{HMoO}_6] \cdot 2\text{H}_2\text{O}$, while in a more alkaline solution the salt $\text{K}_2[\text{Mo}(\text{O}_2)_4]$ is formed.¹⁷ The latter compound is also produced readily by adding potassium molybdate to ice-cold hydrogen peroxide. It is an explosive compound. The sodium and ammonium salts and those of certain metallic amines (*e.g.* of $[\text{Zn}(\text{NH}_3)_4]^{++}$) have also been obtained.

The behaviour of tungstates with hydrogen peroxide is very similar to that of molybdates, derivatives of the two acids $\text{H}[\text{HWO}_6]$ and $\text{H}_2[\text{W}(\text{O}_2)_4]$ being obtained. As in the case of the corresponding permolybdate ion, it is uncertain how $[\text{HWO}_6]^-$ should be formulated. Pertungstates of the type $\text{M}_2^+[\text{W}(\text{O}_2)_4]$, which are formed when normal tungstates (M_2^+WO_4) react with 30 per cent hydrogen peroxide, are somewhat more stable than the corresponding permolybdates. Polytungstates also give rise to various polyper-tungstates, but the constitution of these is unknown.

Hydrogen peroxide reacts with uranyl salts, precipitating an

¹⁶ Jahr and Lothar, *Ber.*, 1938, 71, 894, 903, 1127.

¹⁷ Jahr, *Ref.* 12.

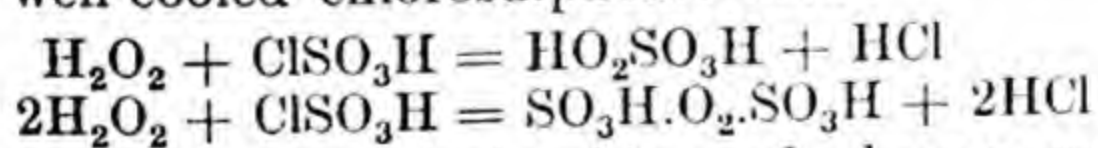
amorphous yellow compound $\text{UO}_4 \cdot 2\text{H}_2\text{O}$ which is remarkably stable and does not lose oxygen until heated above 100° . The structure of this compound has not been finally settled. It cannot be dehydrated without decomposition. The ratio of active oxygen to uranium is 1 : 1, showing that it contains a single peroxy group. The water, however, is constitutional, and may be present partly or wholly as (OH) groups. It does not form salts directly on treatment with bases, though peruranates do result when the freshly precipitated compound is treated with alkali and hydrogen peroxide.

The simultaneous action of alkalis and hydrogen peroxide on uranyl salts leads to the formation of peruranates, which contain more than one atom of active oxygen per atom of uranium. Several series of salts are known, though in no case is there any reliable structural evidence. The chief types are: $\text{R}_2\text{U}_2\text{O}_{10} \cdot n\text{H}_2\text{O}$; $\text{R}_2\text{UO}_6 \cdot n\text{H}_2\text{O}$; $\text{R}_2\text{U}_2\text{O}_{13} \cdot n\text{H}_2\text{O}$ and $\text{R}_4\text{UO}_8 \cdot n\text{H}_2\text{O}$, and it is likely that these compounds bear a general structural resemblance to the permolybdates and pertungstates.

The Persulphuric Acids.

The observation that less than the theoretical quantity of oxygen is evolved at the anode when concentrated solutions of sulphuric acid are electrolysed was made by Faraday in 1832. Meidinger, twenty years later, found that a solution with strong oxidizing properties was produced during the electrolysis, and in 1864 Brodie suggested that it contained a persulphuric acid, and not free hydrogen peroxide, since it did not decolorize permanganate.

There are two per-acids of sulphur, perdisulphuric acid, $\text{H}_2\text{S}_2\text{O}_8$ (Marshall's acid), and permonosulphuric acid (Caro's acid), H_2SO_5 . Both, when pure, are crystalline solids (m.p. 65° and 45° , respectively). Numerous perdisulphates are known, but it is doubtful if the pure salts of permonosulphuric acid have ever been prepared. The pure acids were synthesized by d'Ans and Friederich¹⁸ by the gradual addition of the calculated amount of anhydrous hydrogen peroxide to well-cooled chlorosulphonic acid:

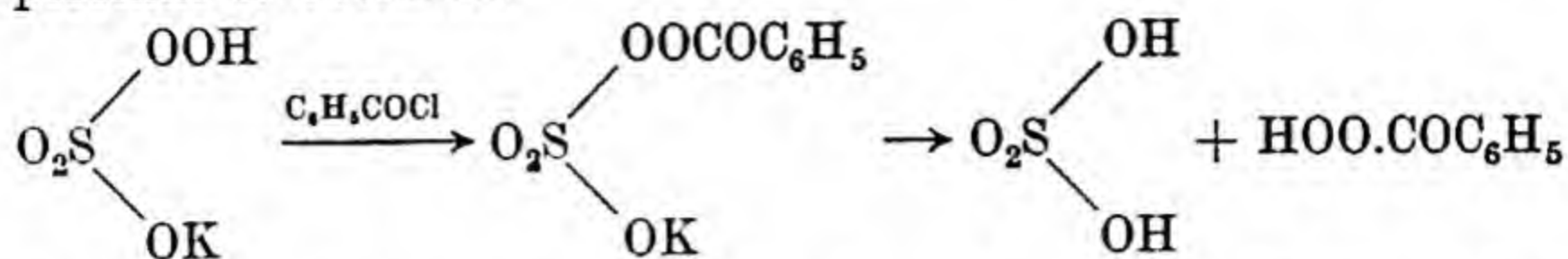


This synthesis shows the relationship to hydrogen peroxide very clearly. Perdisulphuric acid is dibasic, the acidic hydrogen being in the two SO_3H groups. Caro's acid, on the other hand, is monobasic, as the residual hydrogen in the $-\text{O}-\text{O}-\text{H}$ group is too weakly acidic to form salts. Willstätter and Hauenstein¹⁹ were able to prepare the benzoyl derivative of the potassium salt of Caro's acid and showed that it is the hydroperoxide group which is

¹⁸ *Ber.*, 1910, 43, 1880.

¹⁹ *Ibid.*, 1909, 42, 1849.

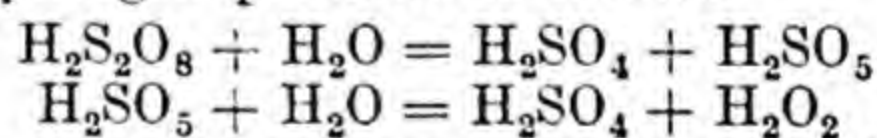
benzoylated since, by acid hydrolysis in ether solution, benzoyl peroxide is obtained.



Any uncertainty as to the structure of perdisulphuric acid is removed by the X-ray analysis of ammonium and caesium perdisulphates,²⁰ which shows that the S_2O_8 ion is formed from two SO_4 tetrahedra, joined by a bond between two oxygen atoms.

The electrolytic method of preparation is used commercially in the preparation of perdisulphates. Usually a concentrated solution of ammonium or potassium sulphate in dilute sulphuric acid is electrolysed in a divided cell with a high anode current density. In the Weissenstein process the anode is a narrow strip of platinum welded to a tantalum bar. The latter rapidly becomes coated with a non-conducting oxide film, which leads to a high current density at the platinum surface. Both the ammonium and the potassium salts are sparingly soluble in water. Perdisulphates are also formed by the action of fluorine on solutions of potassium hydrogen sulphate, though this method has no commercial application.

The hydrolysis of perdisulphates is a reaction of considerable interest. When freshly acidified with sulphuric acid, solutions of perdisulphates have reactions consistent with the presence of $\text{H}_2\text{S}_2\text{O}_8$. The oxidizing power of the solution changes rapidly to that characteristic of Caro's acid, and by taking the reaction one stage further, hydrogen peroxide is formed

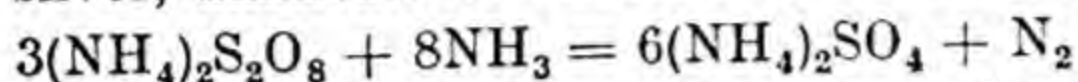


The hydrolysis of perdisulphuric acid successively to Caro's acid and hydrogen peroxide forms the basis of an important technical process for the production of hydrogen peroxide. The electrolyte, consisting either of dilute sulphuric acid or ammonium bisulphate, passes from the electrolytic cells, in which perdisulphate is formed, to some type of high speed vacuum evaporator, in which the per-acid is hydrolysed. Aqueous hydrogen peroxide distils over and the regenerated electrolyte is returned continuously to the cell. The electrolytic oxidation can be conducted with at least 85 per cent current efficiency: the distillation is attended with a loss—from decomposition and incomplete distillation of the hydrogen peroxide—of only about 5 per cent. This process has great advantages over the preparation of hydrogen peroxide from barium peroxide in

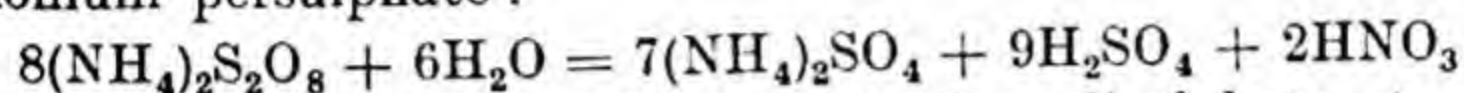
²⁰ Mooney and Zachariasen, *Phys. Rev.*, 1933 (ii), 44, 327.

that the material is obtained in one stage in 30–35 per cent solution which has good keeping qualities owing to its high purity.

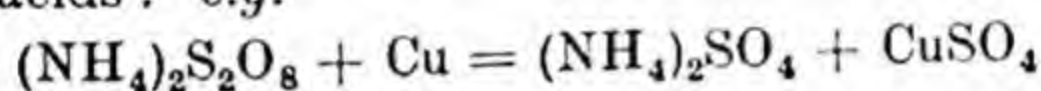
Both perdisulphuric and permonosulphuric acid, as well as their salts, are strong oxidizing agents. They are distinguished from hydrogen peroxide by their failure to react with potassium permanganate. Iodine is liberated at once from potassium iodide by H_2SO_5 , but only slowly by $\text{H}_2\text{S}_2\text{O}_8$. Barium perdisulphate is distinguished from barium sulphate by being soluble in water. Oxidations by perdisulphates are catalysed by silver salts, probably as a result of the intermediate formation of the oxide AgO . In presence of traces of silver, ammonia is oxidized in concentrated solution:



Silver ions also bring about the spontaneous decomposition of ammonium persulphate:

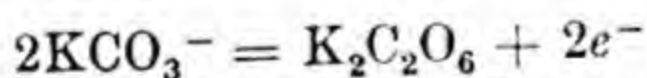


Thiosulphates are oxidized by excess of perdisulphates to tetrathionates or, in the presence of an excess of thiosulphate, to trithionates. Many metals also dissolve in solutions of perdisulphates without evolution of gas, forming their sulphates, or, in the case of amphoteric elements such as chromium and arsenic, the corresponding oxyacids: *e.g.*

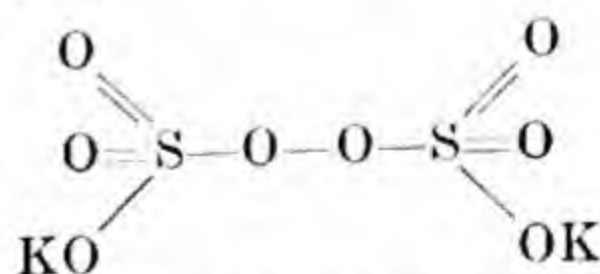
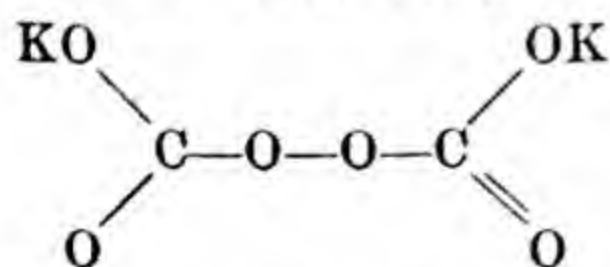


The Percarbonates and Per-acids of Group IV B.

The electrolysis of concentrated solutions of potassium carbonate at -10° with a high anode current density leads to an anode reaction comparable with that involved in the formation of perdisulphates. The product is a pale blue potassium percarbonate, $\text{K}_2\text{C}_2\text{O}_6$, the simplest explanation of its formation being in terms of the reaction: ²¹

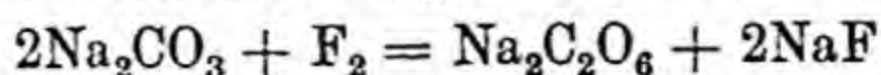


A rubidium salt may be obtained in the same way, but the low solubility of sodium and ammonium carbonates is an obstacle to the electrolytic preparation of percarbonates of these two elements. It is probable that potassium perdicarbonate and perdisulphate have similar structures, as shown below:

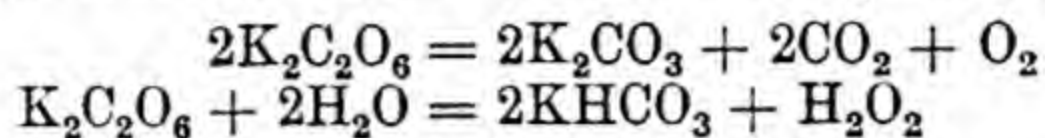


²¹ See, however, Partington and Fathallah, *J.C.S.*, 1950, 1934. This paper contains a valuable review of the literature of the percarbonates and new experiments which elucidate a number of contradictions in earlier work.

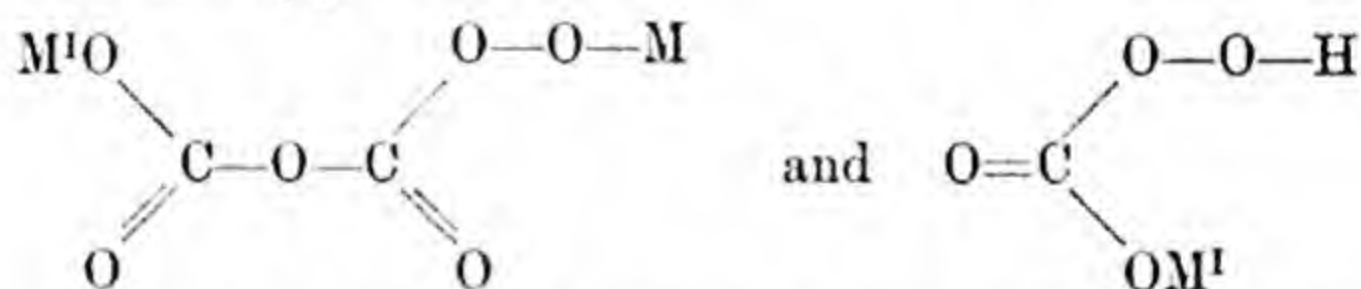
Solutions which are believed to contain analogous percarbonates are obtained by the action of fluorine at *ca.* -15° on solutions of the alkali metal carbonates,²² a possible mode of formation being :



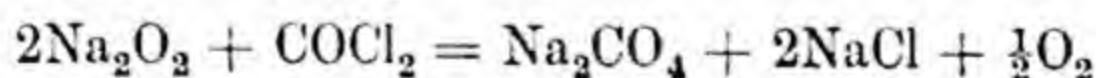
Potassium perdicarbonate decomposes when gently heated, with liberation of carbon dioxide and oxygen. It is slowly hydrolysed by ice-cold water, has strong oxidizing properties and causes the immediate liberation of iodine from neutral potassium iodide.



Another type of percarbonate with the peroxy group differently situated in the molecule was obtained by Wolffenstein and Peltner²³ by the action of carbon dioxide on hydrated sodium peroxide, or a solution of sodium hydroperoxide in absolute alcohol. There is much confusion in the literature as to the exact products of these and a number of similar reactions, but it appears that two main compounds are formed, $\text{Na}_2\text{C}_2\text{O}_6$ and NaHCO_4 , the first of which is isomeric with the electrolytic perdicarbonate. The structures of these compounds have not been determined but it is probable that they are of the types :



Partington and Fathallah²⁴ have also confirmed the existence of percarbonates such as $\text{Na}_2\text{CO}_4 \cdot 1.5\text{H}_2\text{O}$, which may be written structurally as $\text{O}=\text{C}(\text{OM}^{\text{I}})(\text{OOM}^{\text{I}})$, and have confirmed that some of these percarbonates crystallize with hydrogen peroxide of crystallization. The existence of percarbonates with this type of structure is also shown by the formation of Na_2CO_4 in the reaction of phosgene with sodium peroxide.



Of the other elements of Group IV B, only tin and germanium form salts of true per-acids. Hydrogen peroxide reacts with stannic acid to give a perstannic acid $\text{H}_2\text{Sn}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$. The salts $\text{Na}_2\text{Sn}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$ and $\text{K}_2\text{Sn}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$ ²⁵ are formed by the action of hydrogen peroxide on the metastannates.

Solutions of sodium and potassium metagermanates similarly

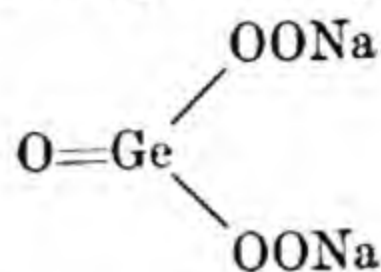
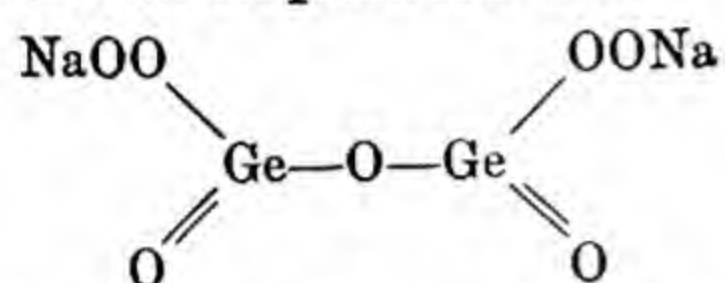
²² Fichter and Bladergroen, *Helv. chim. Acta*, 1927, **10**, 566.

²³ *Ber.*, 1908, **41**, 280.

²⁴ *Loc. cit.*

²⁵ Schwarz and Giese, *Ber.*, 1930, **63**, 781.

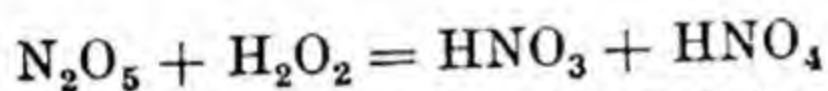
yield the compounds $\text{K}_2\text{Ge}_2\text{O}_7 \cdot 4\text{H}_2\text{O}$ and $\text{Na}_2\text{Ge}_2\text{O}_7 \cdot 4\text{H}_2\text{O}$ when treated with 30 per cent hydrogen peroxide at 0° . These salts are sparingly soluble and from the mother liquor of the sodium salt a second sodium pergermanate, Na_2GeO_5 , may be isolated. These salts may tentatively be assigned the structures below, though it should be emphasized that the evidence is very incomplete.



Lead and silicon probably form no true per-acids; the silicate perhydrates are dealt with in a later section.

Pernitric and Perphosphoric Acids.

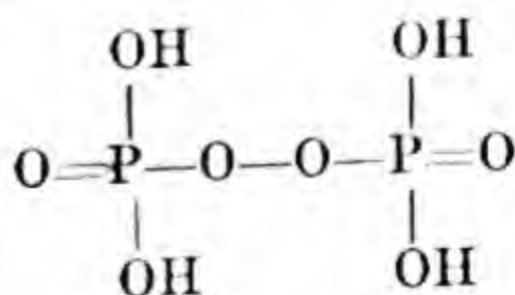
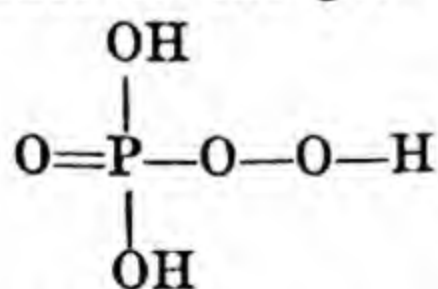
Nitrogen pentoxide reacts with anhydrous hydrogen peroxide at low temperatures forming what is believed to be pernitric acid, HNO_4 .²⁶



The product loses oxygen even at low temperatures and the per-acid cannot be isolated in a pure state, nor have any of its salts been obtained. The product of the original reaction may be stabilized to some extent by the addition of water or glacial acetic acid, and under favourable conditions solutions containing 70–80 per cent of the theoretical yield of pernitric acid may be obtained, as determined by the oxygen evolution on complete decomposition, and by the oxidizing power.

Fichter and Brunner²⁷ state that pernitrates are formed by the reaction of fluorine with 2 per cent solutions of sodium nitrite, but no definite compounds were isolated and this reaction clearly needs closer study. According to Gleu,²⁸ salts of a pernitrous acid HOO.NO are formed by the action of ozone on alkali azides.

Two perphosphoric acids are known, which show a structural resemblance to the persulphuric acids.

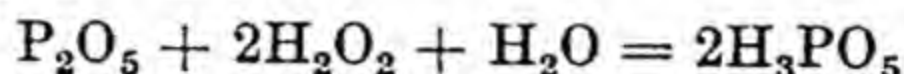


²⁶ d'Ans and Friederich, *Z. anorg. Chem.*, 1911, 73, 344. *Z. Electrochem.*, 1911, 17, 850. FIAT Review of German Science, Inorganic Chemistry, Part I, 1948, 197.

²⁷ *Helv. chim. Acta*, 1929, 12, 305.

²⁸ *Z. anorg. Chem.*, 1929, 179, 233; 1935, 223, 305. Cf. Schmedlin and Massini, *Ber.*, 1910, 43, 1162.

In neither case, however, has the structure been investigated by X-ray methods. Solutions of H_3PO_5 were first obtained by dissolving phosphorus pentoxide in 30 per cent hydrogen peroxide.²⁹ It is possible to moderate the violence of the reaction by using acetonitrile instead of water as a solvent for the hydrogen peroxide. The reaction taking place is :



The formation of perphosphates by anodic oxidation was first realized experimentally by Fichter³⁰ by the electrolysis of a concentrated solution of potassium hydrogen phosphate in the presence of a high concentration of potassium fluoride. Potassium perdisphosphate was isolated by evaporation and crystallization, and from it the barium, zinc, lead and silver salts were obtained. Potassium perdisphosphate is stable in the solid state. Its solutions oxidize aniline to nitrosobenzene and nitrobenzene. In strongly acid solution perdisphosphoric is hydrolysed to permonophosphoric acid in a manner exactly parallel to the formation of Caro's acid from perdisulphuric acid.

Perhydrates.

In a number of instances salts crystallized in presence of hydrogen peroxide are found to contain hydrogen peroxide of crystallization. These are often referred to as perhydrates. When dissolved in water they give the reactions of the normal salt and of hydrogen peroxide. A good example of a perhydrate is the borate $\text{NaBO}_2 \cdot \text{H}_2\text{O}_2 \cdot 3\text{H}_2\text{O}$, which crystallizes under a variety of conditions from alkaline solutions of borax in presence of hydrogen peroxide or sodium peroxide. It is produced technically by the electrolysis of a borax solution containing sodium carbonate. (It may be noted in this connexion that true perborates have not been prepared by electrolysis.) This compound, which is often called sodium perborate, is used extensively in the preparation of washing powders and bleaching agents, and also as a disinfectant. The true perborates $\text{NH}_4\text{BO}_3 \cdot 0.5\text{H}_2\text{O}$ and $\text{KBO}_3 \cdot 0.5\text{H}_2\text{O}$ are precipitated by alcohol from solutions of the corresponding metaborates containing hydrogen peroxide, while the corresponding sodium perborate, NaBO_3 , is formed by the action of boric acid on sodium hydroperoxide, NaO_2H .

Similar hydrogen peroxide addition compounds are formed by some percarbonates, phosphates, silicates and also by compounds

²⁹ d'Ans and Friederich, *Ber.*, 1910, **43**, 1880. Schmedlin and Massini, *ibid.*, 1162. Toennies, *J. Amer. Chem. Soc.*, 1937, **59**, 555.

³⁰ *Helv. chim. Acta*, 1928, **11**, 323.

which have nothing to do with per-acid formation. The latter include compounds such as $\text{Na}_2\text{SO}_4 \cdot 9\text{H}_2\text{O} \cdot \text{H}_2\text{O}_2$, $\text{KF} \cdot \text{H}_2\text{O}_2$, $(\text{C}_2\text{H}_5)_3\text{N} \cdot 4\text{H}_2\text{O}_2$, $\text{CO}(\text{NH}_2)_2 \cdot \text{H}_2\text{O}_2$.³¹ In the case of the carbonates, the position is still somewhat confused because, by the addition of hydrogen peroxide to carbonate solutions, it is possible under some conditions to form true percarbonates, which themselves form perhydrates. It is certain that compounds such as $\text{K}_2\text{CO}_3 \cdot \text{H}_2\text{O}_2 \cdot 1.5\text{H}_2\text{O}$ exist, but doubtful if these are perhydrates of the normal carbonates of the alkali metals.³²

When sodium metasilicate is dissolved in 30 per cent hydrogen peroxide, the perhydrate $\text{Na}_2\text{SiO}_3 \cdot \text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$ is formed. Several similar addition compounds have been obtained from other silicates: it is, however, doubtful if true persilicates have ever been made. A number of perhydrates of alkali metal phosphates have also been described.

³¹ Machu, *Wasserstoffperoxyd und die Perverbindungen*, p. 306.

³² See Partington and Fathallah, *J.C.S.*, 1950, 1934.

CHAPTER XIII

RECENT CHEMISTRY OF METALS

Ion Exchange Resins.

The significance of ion exchange phenomena in minerals and the use of synthetic zeolites for water softening have been familiar to chemists for a long time. In recent years, however, this subject has acquired a much wider significance, particularly in connexion with the separation of the fission products of uranium and of the transuranic elements: it is proposed, therefore, at this point to discuss it briefly.

Natural and synthetic siliceous cation exchange compounds are for the most part aluminosilicates with an open structure which allows a ready flow of ions in and out of the lattice. Certain materials of this type are discussed elsewhere (*see* p. 247). It is possible, however, to make organic resins which have very similar properties and on which, moreover, exchange of either anions or cations can occur. This development has arisen largely from the work of Adams and Holmes,¹ who showed that some synthetic resins formed from phenols and formaldehyde had exchange properties. Similar properties are found in phenol-aldehyde resins containing strongly acidic groups such as $-\text{SO}_3\text{H}$ or $-\text{CO}_2\text{H}$. In these resins, which are hard granular solids, the type of cross linking gives an open molecular structure similar to that in the zeolites and the acidic groups form points of attachment for the cations.

Anion exchange properties are obtained rather similarly, but the most satisfactory resins are those obtained by condensing aromatic amines (*e.g.* *m*-phenylenediamine) with formaldehyde. In these resins there are weakly basic groups ($-\text{NH}_2$ and $-\text{N}=\text{H}$) to which anions can attach themselves. The molecular structure also must be as open as possible to allow free entry and exit of the anions.

The mode of action of either type of resin depends on the differences in the affinity of different ions for the same centre. Perhaps one of the simplest illustrations of the use of these resins is in connexion with the demineralization of water in which cations are first

¹ *J. Soc. Chem. Ind.*, 1935, 1 T; British Patents 450, 308-9 (1934). Duncan and Lister, *Quart. Rev. Chem. Soc.*, 1948, 2, 307; *see also J. Amer. Chem. Soc.*, 1947, 69, 2709-2881.

removed by a cation exchange resin in which the cation is H^+ . Ions such as Ca^{++} and Mg^{++} are taken up and hydrogen ions are released. The anions (*e.g.* CO_3^{--} and SO_4^{--}) are next removed by a bed of base exchange resin giving a product at least as pure as ordinary distilled water.

The factors which determine the relative affinities of the cations in a mixture for the same resin are complex. Valency is important, and as a rule ions of higher valency are more readily adsorbed and less readily removed than those of lower valency. With ions of the same valency differences in affinity are often small, and multi-stage separation processes may be necessary. The problem may be approached in two ways. Firstly the mixture to be separated may be run through the exchange column under conditions such that the different ions concentrate at separated zones in the column. It is not then necessary that any of the ions should pass out of the column (which is usually a vertical glass tube packed with the resin). This is a method commonly used in chromatographic analysis, which, however, depends on adsorption rather than ion exchange. It would be possible in this case to cut up the column and so isolate the contents in the separate zones.

Selective elution offers an alternative method of separation, and is more commonly used. If all the components are first adsorbed on the exchange resin in the column, and a fresh reagent is then passed down the column, the ions may be washed out at different rates and will appear at the bottom of the column at different times with constant flow conditions. The eluting solution is often one capable of forming a complex with some or all of the adsorbed ions. This is well illustrated by work on the separation of the fission products of uranium. These include isotopes of zirconium and niobium, which are very readily removed from trivalent and bivalent fission product ions by eluting with an 0.5 per cent oxalic acid solution, which forms stable oxalate complexes only with the two elements named. The rare earths may be similarly selectively eluted and separated by citrate ions with which they appear to form ill-defined complex ions. This separation is discussed more fully in the next section in considering the isolation of the rare earth promethium.

Promethium.

The search for the missing rare earth element of atomic number sixty-one in nature has been conducted with very great care. In the rare earth series it lies between neodymium ($Z = 60$) and samarium ($Z = 62$), and would be expected to emerge in one or other of the fractional crystallization procedures which have been

developed. Several claims to have detected the new element have been made, though it is very doubtful if any are correct.² They have been based on supposed new lines in the optical emission spectrum of material obtained in fractionally crystallizing rare earth mixtures, on lines in X-ray emission spectra which could be attributed to Element 61, or on supposed new absorption bands in solution.

It is now known that isotopes of Element 61, which has been named promethium, may be produced in nuclear reactions brought about in the cyclotron, and are also formed in the fission of U^{235} . There is still doubt as to the nuclear assignment of some of the activities which have been attributed to promethium, but the following are definitely established :³

<i>Isotope</i>	<i>Half-life and Decay</i>	<i>Mode of Production</i>
Pm^{147}	3.7y., β^-	Nd^{147} , formed in fission (2.6% yield)
Pm^{148}	5.3d., β^- , γ	Nd^{148} (p, n)
Pm^{149}	47h., β^- , γ	U(n, f)
Pm^{153}	< 5m., β^-	U(n, f)
Pm^{156}	< 5m., β^-	U(n, f)

The relatively large amounts of promethium formed in fission make this a suitable source from which to prepare macro quantities for chemical work. The fission products of uranium include, however, over thirty isotopes of yttrium and the rare earth elements from lanthanum up to and including europium. This at once raises the difficult problem of how to separate these various elements. With the conventional methods, depending on differences of solubility or basicity, this would have been a formidable task, but fortunately the new cation exchange resins have simplified the separation and identification procedures very much. Ion exchange separations are also specially suitable for use with radioactive solutions, as they involve a minimum of manipulation and thus reduce the difficulty of shielding the operator from radiation hazards. The principles employed have been outlined already, and it only remains to refer to points of detail relevant to the isolation of promethium.

The exchange resin was of the sulphonated phenol-formaldehyde type (Amberlite IR-).⁴ The order of elution of the rare earths was first established in a series of experiments using radioactive Y, La, Ce, Pr, and Eu and inactive Sm and Nd. It was

² See *Chem. Soc. Ann. Repts.*, 1935, 32, 139; Ballou, *Phys. Rev.*, 1948, 73, 630.

³ Marinsky, Glendenin and Coryell, *J. Amer. Chem. Soc.*, 1947, 69, 2785.

⁴ Ref. 3.

found that it was the reverse of the order of atomic numbers and that unknown isotopes could therefore be identified from the elution curve of a group of earths. Next activities present in the rare earth fission product mixture were examined. Cerium was removed as the sparingly soluble ceric iodate and yttrium, samarium and europium by digestion with potassium carbonate. Then the residue, mixed with a lanthanum carrier, was adsorbed on the resin column and eluted with a 5 per cent solution of ammonium citrate at pH 2.75. Successive fractions of the eluted material were collected and the activity plotted against the volume eluted. The curve shown below was obtained:

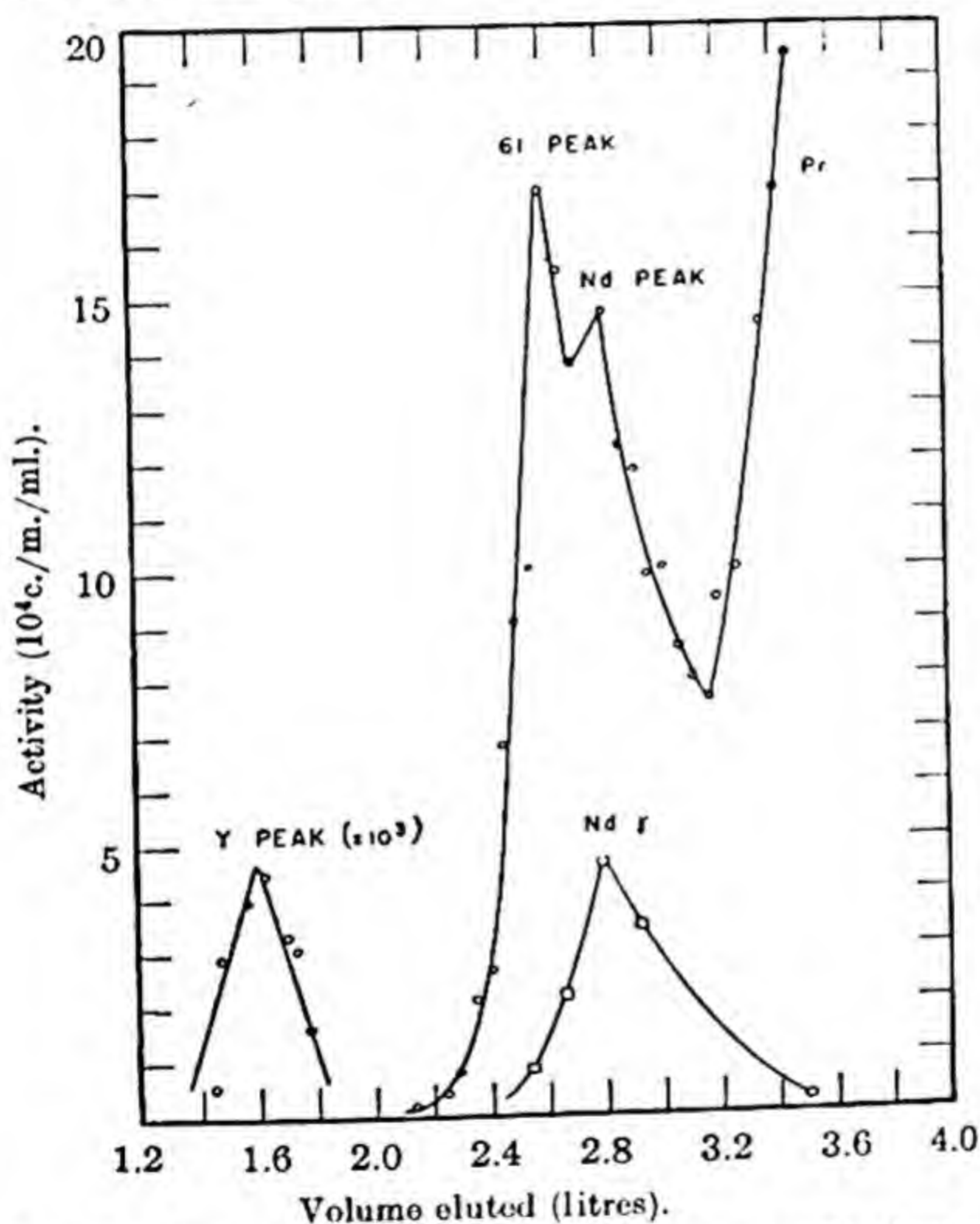


FIG. 58.—Elution curve of intermediate rare earth fraction.

It was known from the preliminary separation that the mixture was likely to contain three main fission products (Pm, Nd and Pr). The first peak activity was identified with the isotope Y⁹¹ (*t*_{1/2}, 57 d). It follows, then, from the order of elution established that the other three are due to Pm, Nd and Pr in that order.

So far little has been published on the chemistry of promethium.

It is fairly certain, however, that it will show no significant differences from the other rare earths and will have a single valency of three. The K and L X-ray emission spectra have been photographed, and the results leave no doubt as to the identity of the new element.⁵

Technetium.

The first well-supported claim to have isolated the missing element of atomic number 43 was made in 1925 by Noddack, Tacke and Berg⁶ in the course of an examination of the X-ray emission spectra of concentrates from platinum ores, columbite, tantalite, gadolinite and various other minerals. Element 75 was found at the same time and the two were named masurium and rhenium, respectively. The subsequent histories have been very different, for, whereas the discovery of rhenium has been amply confirmed and its descriptive chemistry is now known in some detail, the occurrence of masurium in nature has never been independently verified. Indeed it seems probable that the original work was in error and that the more recent work on radioactive isotopes of Element 43, to which the name technetium has now been given, also represents its first discovery.

It is important to examine the supposed isolation of masurium more closely before passing on to the more recent work, as it will be seen that the procedures used were capable of isolating the element. The treatment of a Ural platinum ore will therefore be briefly described as an example. Some 80 grams of the mineral were evaporated to dryness with *aqua regia* and the residue was ignited alternately in hydrogen and in oxygen to drive off all sublimable material. The sublimate separated in zones, corresponding to constituents of differing volatilities and consisting of ruthenium, osmium and arsenic oxides. There was, however, a small amount of sublimate consisting of white needles, which could be resublimed in oxygen at 400° and which blackened in hydrogen sulphide. The quantity was of the order of 1 mg. and it was on such a sample that the X-ray examination for Elements 43 and 75 was carried out.

The K_{α_1} , K_{α_2} and K_{β_1} lines of 43 were identified, the observed wave-lengths being 0.672, 0.675 and 0.601 Å., compared with the values of 0.6734, 0.6779 and 0.600 Å. calculated from Moseley's Law. This agreement is not perfect, and it now seems likely that

⁵ Burkhart, Peed and Spitzer, *Phys. Rev.*, 1949, 75, 86; 76, 143.

⁶ Noddack, Tacke and Berg, *Sitzber. Preuss. Akad.*, 1925, 400; *Naturwiss.*, 1925, 13, 567; Tacke, *Z. angew. Chem.*, 1925, 38, 1157.

these lines were due to overlap with the more complex L spectra of some other element present. The highest concentration of 43 claimed was 0.2–1.0 per cent⁷ in a sulphide concentrate from columbite, and no pure compound was ever isolated.

The artificial production of Element 43 by nuclear reactions was first realized experimentally by Perrier and Segré.⁸ A molybdenum plate was used as a cyclotron target and bombarded with deuterons and secondary neutrons. Sufficient time was allowed for any short-period induced radioactivity to decay and after six weeks the molybdenum still showed a strong activity which was chiefly due to slow β -particles.

The possible artificial radioactive elements which could have been formed from molybdenum under these conditions were: zirconium, niobium, molybdenum and technetium. Of these, zirconium could be produced by fast neutrons, molybdenum and niobium by neutrons or deuterons, and technetium by deuterons. In addition there was the possibility of an activity arising from impurities. The principle used in determining the cause of the activity was to add in turn, to separate portions of a solution of the molybdenum in *aqua regia*, milligram quantities of inactive niobium, rhenium, manganese and zirconium, and then to recover this inactive material by normal analytical procedures. It was found that the activity was consistently separated with rhenium, but not with niobium, zirconium or molybdenum. It was concluded that it was due to a new element (technetium) which was similar chemically to rhenium.

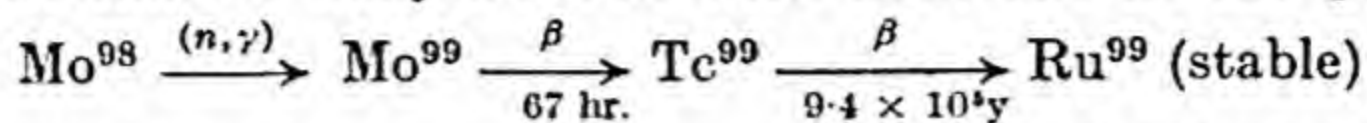
These 'tracer' experiments were carried further. Thus the activity was precipitated from solution with manganous and rhenium sulphides, showing that technetium probably formed an insoluble sulphide under the conditions used. Moreover, when the molybdenum containing technetium was converted to MoO_3 after the addition of some inactive rhenium, and then heated at 550° in oxygen, the rhenium volatilized as oxide and was accompanied by technetium. When thallium perrhenate was precipitated it again carried technetium with it. These and a number of similar experiments conducted with minute amounts of material served to establish the general chemical similarity of the two Group VII elements.

It is now known that at least six radioactive isotopes of technetium can be produced by suitable nuclear reactions. The isotope studied by Perrier and Segré was Tc^{97} , which has an 88-day half-life. The most useful isotope for chemical studies is, however, Tc^{99} , which is

⁷ W. and I. Noddack, *Metallbörse*, 1926, 16, 2129; *Chem. Soc. Ann. Repts.*, 1935, 32, 143.

⁸ *J. Chem. Phys.*, 1937, 5, 712; 1939, 7, 155.

β -active with a half-life of 9.4×10^5 years. This may be produced by the irradiation of molybdenum with neutrons in the pile.



The same isotope is also formed with a yield of 6.2 per cent in the fission of U^{235} . This is a source of macro quantities of technetium. The separation is complicated by the high activity of other fission products present in the uranium, which necessitates the use of heavy screening from radiation when carrying out the separation. Uranium containing the mixture of fission products is first dissolved in hydrochloric acid and the UCl_4 formed is oxidized to UO_2Cl_2 by hydrogen peroxide. The essential step in the separation of technetium from the resulting solution is the addition of platinum chloride and the passage of hydrogen sulphide at 90° . This precipitates platinum sulphide (PtS_2) with the acid-insoluble sulphides of other fission products (including Tc_2S_7). The sulphide precipitate is separated, dissolved in ammoniacal hydrogen peroxide and the solution evaporated to dryness with the addition of bromine. The dry residue is distilled with 18-N sulphuric acid, when technetium distils as the oxide Tc_2O_7 . In order to obtain the technetium in a pure state it is recycled several times through sulphide precipitations and sulphuric acid distillations.

The information at present available on the chemistry of technetium is scanty.⁹ The metal has been prepared by reducing Tc_2S_7 with hydrogen and is found to have a hexagonal close-packed lattice and to be isomorphous with rhenium, ruthenium and osmium. The X-ray emission spectrum has been examined and the wave-lengths found to correspond with those predicted from Moseley's law. It appears that the stability of the +7 oxidation state is greater than that of manganese but less than that of rhenium.

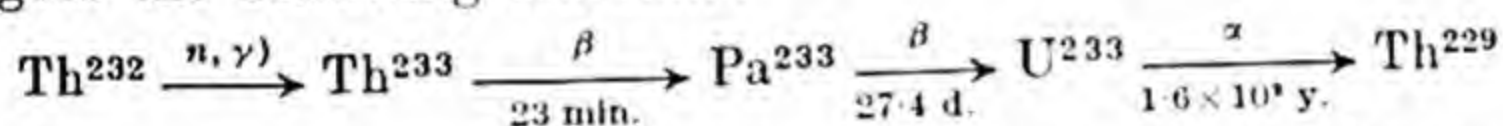
When technetium metal is heated in oxygen at $400\text{--}600^\circ$ a light yellow crystalline oxide (m.p. 119.5°) is formed which has been identified as Tc_2O_7 . This is very hygroscopic and dissolves in water to give a pink solution with the characteristics of a strong monobasic acid. On slow evaporation of the acid solution over sulphuric acid red-black hygroscopic crystals of the acid HTcO_4 separate. Its ammonium salt, NH_4TcO_4 , is stable in air at 100° . The pertechnetate ion shows an intense ultra-violet absorption with maxima at 2470 and 2890 Å., which serves for the detection of as little as 10^{-8} g. Tc. Technetium forms a dark brown sulphide which is

⁹ See Friedlander and Kennedy, *Introduction to Radiochemistry* (John Wiley and Sons, Inc., New York, 1949), p. 270; Boyd, Cobble, Nelson and Smith (unpublished observations).

insoluble in acids, and which, when heated in chlorine, probably forms a volatile chloride. The only evidence for the existence of lower valency states of technetium is that precipitates of MnO_2 and $\text{Mn}(\text{OH})_2$ carry technetium in presence of strong reducing agents. The availability of macroscopic quantities of the element should, however, lead to a rapid advance in our knowledge of its chemistry.

Protactinium.

Among the missing elements at the time when Mendeléeef first drew up the Periodic Table was one preceding uranium, which he named eka-tantalum. This is now known as protactinium (Pa). It was discovered independently by Hahn and Meitner in 1917 and by Soddy and Cranston in 1918, and was recognized as the parent of actinium, which it forms by the loss of an α -particle. This isotope, Pa^{231} , has a half-life of 3.2×10^4 years, but there are others among which the 27.4 day Pa^{233} is specially important. It is a member of the $4n + 1$ series (see p. 536) and is formed by the α -decay of Np^{237} ($t_{1/2}$, 2.2×10^6 y.). A more convenient source, however, is thorium, which, under bombardment with slow neutrons, undergoes the following reaction:



The β -active isotope Pa^{233} is a very useful material for use in studying the chemistry of the element by tracer techniques, as it is easier to obtain and safer to handle than natural Pa^{231} . The chemistry, and especially the valency states, of protactinium are particularly important because of the uncertainty of the relationship to the actinides.

Uranium minerals contain about 8 g. of protactinium per 10 g. of radium. A weighable quantity (2 mg.) was first isolated from pitchblende in 1927 by von Grosse.¹⁰ In 1934 Graue and Käding¹¹ worked up 5.5 tons of Joachimsthal radium residues and obtained 0.5 g. of protoactinium in the form of the salt K_2PaF_7 . At about the same time von Grosse and Agruss¹² isolated a further 0.1 g. of the oxide. The starting material was a pitchblende residue the main constituents of which were:

	%		%		%
SiO_2	60	Al_2O_3	5	MgO	0.5
Fe_2O_3	22	MnO	1	Ti	0.3
PbO	8	CaO	0.6	$\text{Zr} + \text{Hf}$	0.1

¹⁰ *Nature*, 1927, 120, 621; *Ber.*, 1928, 61, 233.

¹¹ *Angew. Chem.*, 1934, 47, 650.

¹² *J. Amer. Chem. Soc.*, 1934, 56, 2200; *Ind. Eng. Chem.*, 1935, 27, 422; see also *Chem. Soc. Ann. Repts.*, 1935, 32, 144.

The protactinium content of this material was 300 mg. of Pa_2O_5 per metric ton, corresponding to a concentration of 1 in 3,000,000. The richest pitchblendes contain about 200 mg. per ton. The three main steps in the large-scale extraction were:

(1) Leaching with hot 25 per cent hydrochloric acid for 2 hours at 95° . This removed the iron, the more basic oxides and most of the lead. The residue consisted of silica together with small amounts of the less basic oxides, notably those of zirconium and titanium. The protactinium concentration in this residue was 1 in 2,000,000.

(2) and (3) The residue was fused with sodium hydroxide, the sodium silicate formed being leached out from the melt, and the solution acidified with hydrochloric acid. The protactinium at this stage was divided between the precipitated silica, which contained about 70 per cent, and the acid liquor, which contained the remainder. From the latter the protactinium was precipitated, together with zirconium, as phosphate by the addition of a zirconium salt and phosphoric acid. Co-precipitation of zirconium with protactinium under these conditions was complete. It was necessary before carrying out this precipitation to add an excess of hydrogen peroxide to convert titanium to pertitanic acid and so prevent its co-precipitation with the zirconium. The coagulated silica residue was treated with 20 per cent sodium hydroxide solution, and the residue dissolved in hydrochloric acid and treated as before for the precipitation of zirconium phosphate. The above operations, starting with 1000 kg. of residues, gave 4.9 kg. of zirconium phosphate containing 250 mg. of protactinium at a concentration of 1 in 20,000. By eliminating phosphoric acid and silica this concentration was further increased to 1 in 5,000, the net recovery being about 75 per cent.

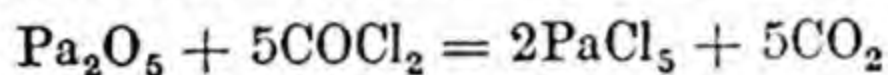
The material obtained from the above large-scale operation may be further concentrated on a laboratory scale by fractional crystallization of zirconium oxychloride from hydrochloric acid, when protactinium is enriched in the solution, or by fractional precipitation of zirconium phosphate. When the protactinium concentration reaches about 10 per cent, the bulk of the zirconium may be removed by sublimation as chloride, while protactinium pentoxide is then precipitated from acid solution by means of hydrogen peroxide.¹³

The separation of protactinium from concentrates may be greatly simplified by adsorption on a manganese dioxide precipitate followed by separation from manganese by an ion exchange resin. Alternatively it may be separated from manganese by conversion to its cupferron complex and extraction of the latter by means of

¹³ Von Grosse and Agruss, *J. Amer. Chem. Soc.*, 1934, 56, 2200.

organic solvents.¹⁴ These newer methods of separation have been worked out with tracer quantities of Pa^{233} , but there seems no reason why they should be not used to isolate larger quantities of the natural isotope Pa^{231} .

The reactions of protactinium pentoxide show it to be basic, whereas the pentoxides of tantalum, niobium and vanadium are acidic or amphoteric. Thus, on fusion of a zirconium-protactinium mixture containing tantalum with potassium carbonate, part at least of the tantalum goes into solution, whereas the protactinium remains in the residue. Protactinium pentoxide is precipitated from sulphuric acid solution by hydrogen peroxide, whereas tantalum pentoxide is not precipitated in this way. The oxides of both elements dissolve readily in hydrofluoric acid and are reprecipitated by ammonia. Treatment of the pentoxide with carbonyl chloride at 550° converts the oxide to the pentachloride



The halide sublimes in almost colourless needles, which melt at 301° and sublime somewhat below this temperature. The crystalline complex fluoride, K_2PaF_7 , has also been prepared by dissolving the oxide in hydrofluoric acid and adding potassium fluoride, and corresponds to the fluorotantalate K_2TaF_7 .

Metallic protactinium was prepared by two methods.¹⁵ In the first the pentoxide supported on a copper target was subjected to electron bombardment in high vacuum, when oxygen was split off, leaving a shiny and partly sintered metallic mass, which was stable in air. Alternatively, decomposition of the vapour of the chloride, bromide or iodide of protactinium on a tungsten filament heated to a high temperature, gave a deposit of the metal.

More recent studies of the chemistry of protactinium¹⁶ have shown that the composition of the supposed pentoxide is probably more correctly represented by the formula $\text{PaO}_{2.25}$ or Pa_4O_9 . When this material is ignited in oxygen at 1100° the pentoxide is formed, while when heated in hydrogen at 1600° the oxide PaO_2 is produced. This dioxide is converted by hydrogen fluoride to a tetrafluoride, PaF_4 , which may be reduced by barium at 1500° to protactinium metal. The oxide PaO forms as a surface contamination on the metal and has been shown to have a rock salt structure. When the metal is heated in hydrogen at $250\text{--}300^\circ$ the interstitial hydride PaH_3 is formed, which resembles UH_3 . This recent work, in which microgram quantities of the element have been used, has confirmed

¹⁴ Maddock and Miles, *J.C.S.*, 1949, S.253.

¹⁵ Ref. 13.

¹⁶ Sellers, Fried, Elson and Zachariasen, *XIIth Int. Congr. Pure Appl. Chem.*, New York, 1951, Abstr., 376.

the formation of a volatile chloride, which is probably PaCl_5 and is reduced by hydrogen at 500° to PaCl_4 . The tetrahalides of protactinium appear to resemble those of thorium, uranium, neptunium and plutonium. The pentoxide is converted by hydrogen sulphide to the compound PaOS , which resembles ThOS , UOS and NpOS . Independent evidence for the formation of an insoluble tetrafluoride has been obtained by Bouissières and Haïssinsky.¹⁷

Astatine.—It is convenient to discuss the production and chemistry of the new halogen element astatine at this point, for although it is not a metal, its mode of production and radioactive properties relate it closely to certain of the heavy radioactive elements. It is fairly certain that astatine does not occur in nature in amounts which have any significance for chemical work. Isotopes occur, however, as short-lived branch products in the uranium and actinium decay series, but the only chemical studies so far reported have been made on material prepared by means of the cyclotron. The isotopes At^{210} , which is prepared from Bi^{209} by an $(\alpha, 3n)$ reaction and decays by K-capture ($t_{1/2}$, 8.3 hr.), and At^{211} , an α - and γ -ray emitter ($t_{1/2}$, 7.5 hr.) prepared by the reaction $\text{Bi}^{209}(\alpha, 2n)\text{At}^{211}$, are the longest lived: the second is more suitable for studying the chemistry of astatine.

The isotope At^{211} was prepared by bombarding a bismuth target with 21–29 Mev helium ions.¹⁸ The choice of particles in this energy range is critical since, above 28 Mev, At^{210} is also produced by an $(\alpha, 3n)$ reaction and its decay by K-capture to Po^{210} introduces an undesirable impurity. Astatine is separated from the target by volatilizing it in vacuum from the melted bismuth, and condensed in a tube cooled in liquid nitrogen. The material collected is dissolved in a drop of nitric acid and washed with distilled water into a stock bottle. The solution chemistry of astatine must be investigated with extremely dilute solutions because of the very high specific activity of At^{211} ($t_{1/2} = 7.5$ hr.). Thus a molar solution would emit 1.54×10^{16} α particles/c.c./sec. and these would lead to rapid decomposition of the water. Most work has therefore been done with solutions which were 10^{-11} – 10^{-15} molar.

Astatine shows its similarity to the halogens by being appreciably volatile from a glass surface even at room temperatures, although it is strongly held on silver. It appears to exist in aqueous solution as the free halogen and may be extracted by carbon tetrachloride or benzene. In establishing this point experimentally

¹⁷ Bouissières and Haïssinsky, *J.C.S.*, 1949, S, 256; *Compt. rend.*, 1948, 226, 573.

¹⁸ Corson, Mackenzie and Segrè, *Phys. Rev.*, 1940, ii, 57, 459; 58, 672; Johnson, Leininger and Segrè, *J. Chem. Phys.*, 1949, 17, 1.

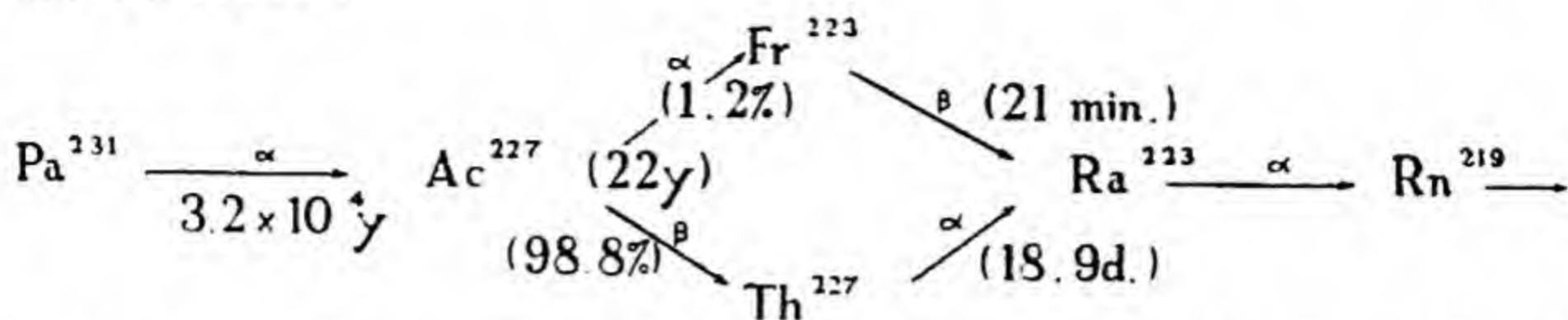
it is necessary only to determine the distribution of α -activity between the two phases. This is a much more sensitive method than any ordinary physical or chemical analytical procedure and is therefore suitable for use with very small quantities of the halogen.

Free astatine is oxidized by hypochlorite or a hot persulphate solution to the AtO_3^- ion. This is shown by ionic migration experiments on the oxidized solution, in which the direction of movement of the astatine is followed by measurements of the radioactivity of the solution. The astatine migrates to the anode. Furthermore if silver iodate is precipitated in the oxidized solution it carries the astatine with it. There is some evidence that weaker oxidizing agents (*e.g.* bromine) produce the AtO^- ion, but this has not been so clearly established. On reduction by sulphur dioxide the astatide ion, At^- , is formed. This has been shown to migrate to the anode and is also carried completely by silver iodide. There is no evidence as yet that astatine forms a cation or has reactions similar to those of positive iodine, but it must be remembered that the scope of experimental work is very limited, the short half-life making it unlikely that macroscopic quantities will ever be available. The general similarity to the halogens has, however, been established by the experiments described above, and will no doubt be further demonstrated in the future.

Francium.—There have been a number of investigations designed to isolate the heaviest of the alkali metals, which is now known as francium, from natural sources. It would, for example, be expected to form an alum less soluble than caesium alum, since the solubility of the alkali metal alums decreases progressively from sodium to caesium. Fractional crystallization of mixtures of alums obtained from minerals rich in caesium has, however, always given inconclusive or negative results when either the X-ray emission spectrum or the radioactivity of the tail fractions of alum crystallizations has been examined.

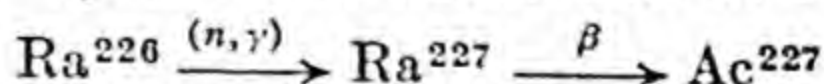
The three classical decay series all have α -active isotopes of radium ($Z = 88$) in their main decay chains, leading to a radon isotope ($Z = 86$), so that Element 87 is not formed. It could, however, be produced by the β -decay of a radon isotope or the α -decay of an isotope of actinium ($Z = 89$). There is no evidence that radon isotopes are anything but α -active, but it was found by Paneth in 1914 that in the actinium series the isotope Ac^{227} , which decays mainly by β -particle emission, also emits some α -particles. It was not certain at the time that this was a true decay of actinium itself, which is difficult to obtain free from other radioactive substances, and the matter was not settled until recently, when

Mlle Perey¹⁹ showed clearly that Ac^{227} decays in two ways, as shown below :



The francium isotope has a half-life of 21 mins., and the method of investigation was to allow a purified actinium solution to decay until the 21 min. activity had reached an almost constant value and then determine the carriers with which it was coprecipitated. It was shown that it was not precipitated with CeO_2 , PbS or BaCO_3 . When, however, a small amount of a soluble caesium or rubidium salt was added to the active solution and then precipitated (as the insoluble perchlorate, picrate, hexachloroplatinate, chlorobismuthate, $\text{M}^1_2\text{BiCl}_5 \cdot 2.5\text{H}_2\text{O}$, or chlorostannate) part or all of the 21 min. activity was always coprecipitated with the alkali metal. Thus, though there is little possibility of isolating the new alkali metal or its salts in weighable quantities, it has been clearly shown that it resembles the two heavy alkali metals in its precipitation reactions. As in the case of astatine which has already been described, the great sensitivity of methods for detecting radioactivity enable this fact to be established on quantities far smaller than would be needed for normal microchemical experiments.

Other francium isotopes have been produced artificially. The isotope Fr^{221} , for example, occurs as a product of the α -decay of Ac^{225} in the new $4n + 1$ series (cf. p. 536). It decays by α -particle emission ($t_{1/2}$, 4.8 min.) forming the short-lived α -active astatine isotope At^{227} ($t_{1/2}$, 0.02 sec.). More important, however, is the production of Ac^{227} by neutron irradiation of radium



Produced in this way, actinium is much more readily freed from other radioactive elements than when it is worked up from naturally occurring sources. The decay of Ac^{227} so obtained gives a very convenient source of material for further work on the new alkali metal.

Polonium.

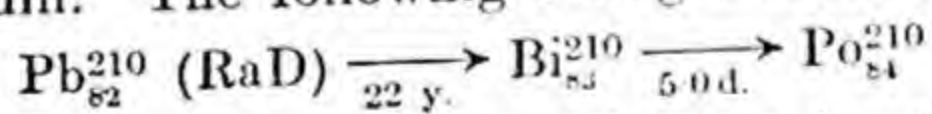
At the present time numerous isotopes of polonium are known. All are radioactive, emit α -rays, and, with the exception of Po^{210} ,

¹⁹ *J. Phys. Radium*, 1939, **10**, 435; Perey and Lacombe, *ibid.*, 1939, **10**, 439; Perey, *J. Chim. Phys.*, 1946, **43**, 155.

which has a half-life of 140 days, are short-lived. The isotope Po^{210} , which is also known as radium F, is a member of the uranium decay series and decays to the stable end product Pb^{206} . One artificial isotope, Po^{209} , a member of the $(4n + 1)$ decay series, has a half-life of about 200 years. Such information as we have on the chemistry of the element has, however, been obtained with Po^{210} .

Polonium was discovered in 1898 by Madame Curie as a constituent of Joachimsthal pitchblende. In its isolation from this source the ore is broken down by roasting with sodium carbonate, excess of the latter being removed by leaching with warm water. Treatment with dilute sulphuric acid dissolves the uranium and leaves a residue which contains lead, calcium, barium, radium and other heavy metals. Included among the latter is polonium. The next stage in the treatment consists essentially in leaving the radium in the residue, in the form of its insoluble sulphate, by digestion with hydrochloric acid. Treatment of the hydrochloric acid solution with hydrogen sulphide then precipitates the sulphides of polonium, bismuth, copper, lead, antimony and arsenic, while a third active precipitate containing actinium and the rare earths is formed by oxidizing the filtrate from the sulphide precipitation with chlorine and adding ammonia. Further concentration is greatly facilitated by the fact that the element is deposited quantitatively from its solutions on a rod of a metal such as silver, copper or nickel. It has a very low deposition potential.

The separation of polonium concentrates is more conveniently carried out by starting from RaD, a lead isotope which is intermediate in the decay series between Ra and Po, and allowing it to grow into polonium. The following changes occur:



The lead isolated from uranium minerals contains the RaD, and when it is stored, becomes richer in polonium. The latter may be separated from time to time from the lead solution either by electrolysis or by deposition on to a metal foil (*e.g.* Ag). The 'active deposit' in old radon tubes is also a very convenient source of RaD and Po. It is dissolved in an acid and the polonium is then deposited on to a metal introduced into the solution.

Polonium may also be produced by irradiating bismuth with neutrons, large fluxes of which are available in atomic piles. The nuclear reaction is: $\text{Bi}^{209}(n, \gamma) \rightarrow \text{Bi}^{210} \xrightarrow{5.0 \text{ d.}} \text{Po}^{210}$. The bismuth used is in the form of pelleted bismuth oxide which, after irradiation, is dissolved in hydrochloric acid. Tellurium chloride is added to the acid solution and, on treatment with stannous chloride,

elementary tellurium is precipitated and carries the whole of the polonium with it. The precipitate is not appreciably contaminated with bismuth. It is dissolved in hydrochloric acid with the addition of an oxidizing agent, and from the resulting solution hydrazine or sulphur dioxide precipitates tellurium. Under these conditions the tellurium does not carry down polonium, which remains in solution and may be deposited on a metal foil in the usual way. This procedure may furnish material for macrochemical studies of the element and its compounds.

Most of our fragmentary knowledge of the chemistry of polonium has up to the present been obtained in experiments employing very small quantities. The chemical properties show some points of resemblance to bismuth and tellurium. The sulphide is less soluble than the sulphides of bismuth or lead and is more volatile than bismuth sulphide. Polonium compounds are also readily hydrolysed and reduced. The element forms an insoluble hydroxide and also a volatile hydride (*see* p. 291). The normal potential calculated for the electrode Po/Po^{4+} in the concentration range 10^{-8} – 10^{-9}N is $+0.77$ volts. It thus lies between tellurium and silver in the electrochemical series.²⁰

A good deal of information has been obtained by applying the principles of isomorphism, according to which, from the isomorphous crystallization of polonium with salts of known formula, the formation of a polonium compound of similar formula may be inferred. It is necessary here to distinguish clearly between adsorption and true isomorphism. Consider, for example, a solution of polonium and tellurium in hydrochloric acid to which stannous chloride is added to precipitate tellurium. It is found that over a range of acid concentrations and for different values of the Po/Te ratio the ratio :

$$\frac{\text{Po : Te in the precipitate}}{\text{Po : Te in the mother liquor}} = \text{a constant}$$

This is regarded as a case of isomorphism, where polonium is incorporated in the tellurium lattice. If, on the other hand, barium chloride is added to an acid polonium solution and barium sulphate is precipitated by adding sulphuric acid, the amount of polonium carried by the precipitate becomes less as the acidity of the solution is increased. This is a case of adsorption. The differentiation of these two effects is not, however, always clear and evidence of this sort must be viewed critically. In all such experiments the polonium concentrations are measured directly by determining the activity of the solid and solution.

²⁰ Coche, Faraggi, Avignon and Haïssinsky, *J. Phys. Radium*, 1949, 10, 312.

The information gained in this way enables the formulæ of certain polonium compounds to be written with some degree of certainty. Thus sodium telluride was prepared by the action of a solution of sodium hyposulphite, $\text{Na}_2\text{S}_2\text{O}_4$, on tellurium containing polonium. The distribution coefficient of polonium between the sodium telluride crystals and the mother liquor was constant, indicating the existence of the compound Na_2Po , isomorphous with Na_2Te .²¹ As an extension of this work it was shown that polonium dibenzyl, $\text{Po}(\text{CH}_2\text{C}_6\text{H}_5)_2$, and tellurium dibenzyl, $\text{Te}(\text{CH}_2\text{C}_6\text{H}_5)_2$, were also isomorphous and that polonium formed a volatile methyl derivative, PoMe_2 . Indications have also been obtained that polonium may form a volatile carbonyl.²²

The work of Guillot²³ leads to the conclusion that polonium can also have valencies of three and four. Thus addition of sodium thiocarbamate to a solution of polonium and a bismuth salt gives a precipitate which is believed to contain the thiocarbamate of trivalent polonium, with a co-ordination number of six. Polonium is believed to be trivalent also in the compound $(\text{NH}_4)_3\text{PoCl}_6 \cdot \text{H}_2\text{O}$, which is isomorphous with the corresponding iridium compound. The compound $(\text{NH}_4)_2\text{PoCl}_6$ is also isomorphous with the corresponding complex salts $(\text{NH}_4)_2\text{PbCl}_6$, $(\text{NH}_4)_2\text{TeCl}_6$ and $(\text{NH}_4)_2\text{SnCl}_6$ in presence of excess of chlorine, and with $(\text{NH}_4)_2\text{PtCl}_6$ even in absence of chlorine. In these cases the element is believed to be quadrivalent. Polonium acetylacetonate has been studied by Servigne,²⁴ who found that the hydroxide was soluble in acetylacetone, the evaporated product being soluble in chloroform, benzene, alcohol or acetone. When the mixed acetylacetonates of thorium, aluminium and polonium were fractionally crystallized, the polonium separated with the thorium, which again shows that, under these particular conditions, polonium was probably quadrivalent. The electrochemical behaviour also accords with the existence of two valency states, the element passing from one to the other with comparative ease.

Fragmentary information on the polonium complexes is obtainable by ion migration experiments. In very dilute acid solutions (e.g. 0.05N HCl or HNO_3) most of the polonium migrates to the cathode, whereas in HCl of strength 0.2N, or in HNO_3 of strength 2N, it goes to the anode. The behaviour in sulphuric acid is similar. It must be emphasized again that such experiments are done with minute amounts of material. They do, nevertheless, give a clear

²¹ Chlopin and Samartseva, *Compt. rend. Acad. Sci., U.R.S.S.*, 1934, 4, 433.

²² Curie and Lecoq, *Compt. rend.*, 1931, 192, 1453.

²³ *Compt. rend.*, 1930, 190, 127, 590; *J. Chim. Phys.*, 1931, 28, 14, 92.

²⁴ *Compt. rend.*, 1933, 196, 264.

indication of complex formation, possibly involving such ions as $\text{Po}(\text{NO}_3)_6^{--}$ and $(\text{PoCl}_6)^{--}$. Some experiments with macroscopic quantities of polonium have already been carried out.²⁵ These include a determination of the crystal structure of the metal, prepared by electro-deposition on platinum foil from a dilute nitric acid solution of polonium nitrate. There were indications from an abrupt change in electrical resistance near 100° that the metal exists in two allotropic forms. It melted at about $240\text{--}255^\circ$.

The Transuranic Elements.²⁶

The following transuranic elements are known at present :

93	Neptunium	Np	96	Curium	Cm
94	Plutonium	Pu	97	Berkelium	Bk
95	Americium	Am	98	Californium	Cf

The methods by which certain of their isotopes are prepared are described later (p. 535) : at this point, however, it is convenient to discuss their chemistry in so far as it has been elucidated. The outstanding point of interest, which arises naturally from the fact that these elements represent an extension of the Mendeleef periodic table, is whether the transuranics are part of a new group of transition elements analogous to the three well-established groups, or of a new group analogous to the rare earths. The physical and chemical evidence available favours the second view.

Any structural analogy between the transuranic elements and the rare earths implies that some of the $5f$ orbits are occupied in the former, just as the $4f$ orbits are occupied in the rare earths. The natural place for this process to commence would be in thorium since the preceding element, actinium, is similar chemically to lanthanum, which has no electrons in its $4f$ shell. The four valency electrons of thorium, however, are known from spectroscopic data to have the $6d^2 7s^2$ configuration. The configuration for protactinium is unknown, but that of uranium may be $5f^3 6d^1 7s^2$.²⁷ There is therefore an *a priori* case for supposing that, in the elements which follow, the $5f$ shell is progressively filled and that it would be half filled in curium, which should be the analogue of gadolinium.

The absorption spectra of compounds of the transuranics resemble those of the rare earths. In the latter the ions are coloured and show abnormally sharp absorption bands due to electron transitions among the $4f$ levels. The sharpness is due to these levels being shielded by $5s$ and $5p$ electrons from distortion by the fields of

²⁵ Maxwell, *J. Chem. Phys.*, 1949, 17, 1288.

²⁶ See Lister, *Quart. Rev. Chem. Soc.*, 1950, 4, 20. Data have been quoted from this source, which gives further details of the chemistry of the transuranic elements.

²⁷ Kiess, Humphreys and Laun, *J. Res. Nat. Bur. Standards*, 1946, 37, 57.

surrounding molecules. An exactly parallel effect is observed for uranium and the elements which follow it. The bands are particularly sharp in the absorption spectra of the few solid crystalline compounds of the transuranics which have been examined.

The magnetic properties of the ions of the transuranic elements may be consistent with the presence of $5f$ electrons, since there is an apparent correspondence between their moments and those of ions of the rare earth elements with the same number of electrons above the rare gas core. The following data illustrate this point. The moments are given in Bohr magnetons.

<i>Ion</i>	<i>No. of electrons above Rn core</i>	<i>Moment</i>	<i>Ion</i>	<i>No. of electrons above Xe core</i>	<i>Moment</i>
NpO_2^{2+}	1	2.40	Ce^{3+}	1	2.39
NpO_2^{+}	2	2.96	Pr^{3+}	2	3.46
PuO_2^{2+}	2	2.95			
U^{4+}	2	2.91	Nd^{3+}	3	3.52
U^{3+}	3	3.20			
Np^{4+}	3	3.03			
Pu^{4+}	4	1.85	Sm^{3+}	5	1.58
Pu^{3+}	5	0.90			
Am^{3+}	6	0.8			

The ionic radii of all the transuranic elements except curium are now known with some certainty as a result of X-ray determinations of the structures of a number of compounds. These show a decrease as the series is ascended which parallels the lanthanide contraction in the rare earth series. The size of an ion is determined by the position of the outermost electrons, and in the rare earth series it is believed that the contraction is due to a progressive drop in the effective nuclear charge (the nuclear charge minus the screening effect of the other electrons). This implies that the screening effect of an extra electron in the $4f$ shell is less than that of an extra electron in the outer orbits and that consequently the outer electrons are progressively more strongly attracted as we pass from cerium to lutecium, with a consequent contraction in the ionic radius.

Table 1

Contraction in Ion Size in Rare Earths and Transuranic Elements

Radius of trivalent ion in Å.	$\left\{ \begin{array}{l} \text{Ac} \\ \text{La} \end{array} \right.$	$\left\{ \begin{array}{l} \text{Th} \\ \text{Ce} \end{array} \right.$	$\left\{ \begin{array}{l} \text{Pa} \\ \text{Pr} \end{array} \right.$	$\left\{ \begin{array}{l} \text{U} \\ \text{Nd} \end{array} \right.$	$\left\{ \begin{array}{l} \text{Np} \\ \text{Pm} \end{array} \right.$	$\left\{ \begin{array}{l} \text{Pu} \\ \text{Sm} \end{array} \right.$	$\left\{ \begin{array}{l} \text{Am} \\ \text{Eu} \end{array} \right.$
	1.11 1.04	— 1.02	— 1.00	1.04 0.99	1.02 —	1.01 0.98	1.00 0.97
Radius of quadrivalent ion in Å.		Th	Pa	U	Np	Pu	Am
		0.95	—	0.89	0.88	0.86	0.85

The transuranics are seen to show a very similar contraction and this is consistent with the preferential filling of the $5f$ orbits in the series.

The Chemistry of the Transuranic Elements.—The valencies of the transuranic elements known at present are summarized below, together with those of the corresponding rare earths.

Valencies of Transuranic Elements and Rare Earths

<i>Element :</i>	<i>Ac</i>	<i>Th</i>	<i>Pa</i>	<i>U</i>	<i>Np</i>	<i>Pu</i>	<i>Am</i>	<i>Cm</i>	<i>Bk</i>	<i>Cf</i>
				6	6	6	6			
			5	5	5	5				
Valency		4	4	4	4	4	4		4	
	3	3		3	3	3	3	3	3	3
		2					2			
<i>Element :</i>	<i>La</i>	<i>Ce</i>	<i>Pr</i>	<i>Nd</i>	<i>Pm</i>	<i>Sm</i>	<i>Eu</i>	<i>Gd</i>	<i>Tb</i>	<i>Dy</i>
			5?							
Valency		4	4						4	
	3	3	3	3	3	3	3	3	3	3
						2	2			

The striking point about this table is that the elements between actinium and curium all have valencies greater than three. The most stable valency of thorium is four, indeed only recently have the di- and tri-iodides been prepared. The valencies of protactinium are still rather uncertain, but the most stable valency is probably five. Uranium is most stable in the sexavalent state and in the elements which follow the lower valency states become progressively more stable, until in curium, the analogue of gadolinium with the configuration $5f^7$, there is, as far as is known at present, a single valency of three. Americium is interesting in that there is definite evidence (*vide infra*) of a bivalent state. The only published work on berkelium and californium shows the valencies tabulated above. The higher valencies of the transuranics compared with the rare earths may be attributed to the fact that the $5f$ electrons are less firmly bound than the $4f$. This was predicted by Bohr in 1922.

The elements of the transuranic series are all base metals and form simple hydrated ions in aqueous solution. In this respect they differ sharply from the platinum metals which are noble and have little tendency to form simple cations. The ions and oxy-ions known to exist in solution are shown in the table below.

		UO_2^{2+}	NpO_2^{2+}	PuO_2^{2+}	AmO_2^{2+}	
		UO_2^+	NpO_2^+	PuO_2^+		
	Th^{4+}	U^{4+}	Np^{4+}	Pu^{4+}		
Ac^{3+}		U^{3+}	Np^{3+}	Pu^{3+}	Am^{3+}	Cm^{3+}
					Am^{2+}	

The solution chemistry of actinium has been little studied, but it is fairly certain that the hydrated Ac^{3+} ion is the normal state.

Thorium forms a number of stable salts, such as the nitrate, $\text{Th}(\text{NO}_3)_4$. The tri-iodide is decomposed by water with liberation of hydrogen. Protactinium is little known at present, but there is evidence of valencies of five and four.

The most stable series of uranium salts is that derived from the uranyl ion, UO_2^{2+} . This, for example, occurs in the familiar compound uranyl nitrate, $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. Electrolytic reduction of solutions containing the uranyl ion leads first to the unstable ion UO_2^+ , which disproportionates readily to U^{VI} and U^{IV} ; further reduction gives U^{4+} and U^{3+} .

Neptunium forms a similar series of ions, but the NpO_2^+ ion is more stable and oxidation of the Np^{IV} to Np^{VI} requires a stronger oxidizing agent than in the case of U^{IV} to U^{VI} . In plutonium this trend is continued, Pu^{IV} being the most stable state, while PuO_2^+ is intermediate in stability between UO_2^+ and NpO_2^+ . These relative stabilities are well illustrated by the oxidation-reduction potentials in $\text{M}-\text{HCl}$ relative to the normal hydrogen electrode. The smaller negative value for the potential indicates that the oxidized state of the couple is relatively more stable.

Couple	U	Np	Pu
III/IV . . .	+ 0.63	— 0.14	— 0.97 volts
IV/V . . .	— 0.55	— 0.74	— 1.13
V/VI . . .	— 0.06	— 1.14	— 0.91

The position of americium is still somewhat uncertain. It is oxidized in alkaline solution by sodium hypochlorite, but it is uncertain whether Am^{IV} or Am^{V} results. The oxide AmO_2 is, however, well known. Sodium amalgam also reduces Am^{III} , the product being almost certainly Am^{II} , as in the reduced state americium is coprecipitated with europous and samarous sulphates. Evidence for the existence of Am^{VI} has been obtained by the synthesis of $\text{Na}(\text{AmO}_2)(\text{CH}_3\text{CO}_2)_3$.

Compounds of the Transuranic Elements.—Although in the main very small quantities of the transuranic elements have been available, remarkable progress has been made in elucidating the descriptive chemistry of their compounds. This has been due largely to the successful application of microchemical techniques and to the use of X-ray structure determinations as a means of characterizing compounds.

The metals neptunium, plutonium and americium are all formed by reduction of the tri- or tetrafluorides by barium vapour at

1200°. They resemble metallic uranium. The oxides which are known at present are shown below.

UO	NpO	PuO	AmO	(Cm ₂ O ₃)
		Pu ₂ O ₃		
		Pu ₄ O ₇		
UO ₂	NpO ₂	PuO ₂	AmO ₂	
U ₄ O ₉				
U ₃ O ₈	Np ₃ O ₈			
UO ₃				

It is probable that the oxides of the transuranics will be more complex than this table indicates: certainly in the case of uranium this is so, as is shown by recent work on the U—O₂ system. The monoxides are formed by vigorous reduction of the higher oxides. The members of this series are isomorphous and have a sodium chloride-type lattice. The compound Pu₂O₃ is formed by heating PuO₂ to 1700°. The dioxides are isomorphous and have the fluorite type of lattice. All except UO₂ are the normal products of ignition of other oxides in air or of decomposition of salts such as the nitrates in air. The oxide UO₃ appears to stand alone, and reflects the higher stability of the sexavalent state in uranium.

The tri- and tetrahydroxides of neptunium, plutonium, and americium are precipitated on adding alkali to solution of the tri- or tetravalent salts: U(OH)₃ and Np(OH)₃ are very readily oxidized. In the sexavalent state Np, Pu and Am show acidic properties, and resemble uranium, which, when ammonia is added to a solution of a uranyl salt, yields ammonium diuranate, (NH₄)₂U₂O₇, or more complex anions (*cf.* dichromates and polychromates). There is a distinct difference in the reactions of uranyl and plutonyl solutions with hydrogen peroxide. The former give a peroxide UO₄·2H₂O (*see p.* 379). Plutonyl solutions, on the other hand, are reduced by hydrogen peroxide to Pu^{IV}, peroxy derivatives of this state being formed which may be similar to the peroxy derivatives of quadrivalent thorium.

The decrease in stability of the higher valency states as the series is ascended is well marked with the halides. Uranium forms both a hexafluoride and a hexachloride, neptunium is known only to form a hexafluoride and there is some doubt whether in the case of plutonium the hexafluoride is formed. The tetrahalides of uranium and neptunium are likewise well known, but only the tetrafluoride of plutonium has been prepared. The trihalides of all of the transuranic elements have been characterized. There are also a number of complex halides of uranium, neptunium and plutonium. The remaining salts of these elements conform to the general pattern

which has been outlined. A number are as yet unknown, but the gaps are rapidly being filled. The main uncertainties at present lie in the questions of which higher valency states of americium will be found to give definite compounds and what compounds will be formed by the very recently discovered elements berkelium and californium.

CHAPTER XIV

METALLIC CARBONYLS, NITROSYLS AND RELATED COMPOUNDS

The metallic carbonyls constitute a group of compounds which occupies a position of peculiar interest in the chemistry of the metals. The carbonyls are characterized by their striking physical properties—*e.g.* their volatility—and their constitution has presented a difficult and controversial problem from the standpoint of theories of valency, since they and their derivatives appear to represent a unique class of compound in which ‘principal valencies’ are not operative. The carbonyls are unique also amongst complex compounds in that their composition is governed, not by considerations of the stable co-ordination numbers of the metals concerned, but, primarily, by the tendency to form closed electronic shells.

A considerable body of modern work, emanating almost entirely from Hieber and his school, has shown that the property of forming carbonyls, or the carbonyl halides related to them, is common to the elements of the transition series from Group VI to Group IB inclusive, as indicated below. The formulæ and the physical properties of all the known metal carbonyls are summarized in Table 1.

V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Nb	Mo	Ru	Rh	Pd	Ag	Cd	Cd
Ta	W	Os	Ir	Pt	Au	Hg	Hg

Metals enclosed ————— form carbonyls.
 Metals enclosed - - - - - form carbonyl halides.

The discovery of this group of compounds was made in 1888–90, when Mond and Langer, investigating the catalytic effect of nickel on the reaction $2\text{CO} \rightleftharpoons \text{C} + \text{CO}_2$, observed that carbon monoxide burned with a greenish, highly luminous flame after it had been passed over reduced nickel.¹ When the gas was passed through a heated tube, metallic nickel was deposited in the form of a mirror, and by cooling the gas with a freezing mixture, the colourless liquid nickel carbonyl, $\text{Ni}(\text{CO})_4$, was eventually isolated. Although, as was later found by Mond, Hirtz and Cowap,² reduced cobalt also

¹ *J.C.S.*, 1890, 57, 749.

² *Ibid.*, 1910, 97, 798.

Table 1

Carbonyls and Carbonyl Hydrides

Cr (24)	Mn (25)	Fe (26)	Co (27)	Ni (28)
Cr(CO) ₆ , sublimes, rhombic, colourless	—	Fe(CO) ₅ , m.p. — 20°, b.p. + 103°, yellow ; Fe ₂ (CO) ₉ , decomp. 100°, yellow, triclinic ; Fe ₃ (CO) ₁₂ , decomp. 140°, green, monoclinic	Co ₂ (CO) ₈ , m.p. 51°, orange-red ; Co ₄ (CO) ₁₂ , decomp. 60°, black, crystalline	Ni(CO) ₄ , m.p. — 25°, b.p. + 43°, colourless
		Fe(CO) ₄ H ₂ , m.p. — 70°, colourless	Co(CO) ₄ H, m.p. — 26°, yellow	
Mo (42)	Tc (43)	Ru (44)	Rh (45)	Pd (46)
Mo(CO) ₆ , sublimes, rhombic, colourless	—	Ru(CO) ₅ , m.p. — 22°, colourless ; Ru ₂ (CO) ₉ , orange, monoclinic ; Ru ₃ (CO) ₁₂ , green needles	Rh ₂ (CO) ₈ , orange, cryst., m.p. 76° (decomp.) ; [Rh(CO) ₃] _n , red, cryst. ; [Rh ₄ (CO) ₁₁] _n , black Rh(CO) ₄ H, m.p. — 10°, pale yellow	—
W (74)	Re (75)	Os (76)	Ir (77)	Pt (78)
W(CO) ₆ , sublimes, rhombic, colourless	Re ₂ (CO) ₁₀ , colourless, m.p. 177°, sublimes, monoclinic	Os(CO) ₅ , colourless, m.p. — 15° ; Os ₂ (CO) ₉ , bright yellow, sublimes, m.p. 224°	Ir ₂ (CO) ₈ , yellow-green, crystalline, sublimes ; [Ir(CO) ₃] ₂ , canary yellow, decomp. 210°, rhombohedral	
	Re(CO) ₅ H (?)	Os(CO) ₄ H ₂	Ir(CO) ₄ H	

combines with carbon monoxide under high pressures, no cobalt carbonyl is formed at atmospheric pressure, so that a complete separation of nickel from accompanying cobalt is achieved by conversion of the nickel to nickel carbonyl. This means of purifying nickel was turned to technical account by Mond for the extraction and refining of nickel from the copper-nickel matte produced from the Sudbury (Ontario) sulphide ore. The crude metal, reduced under controlled conditions, is subjected to the action of carbon monoxide, forming nickel carbonyl. The circulating gases pass into 'decomposers', maintained at $180-200^{\circ}$, which contain pellets of nickel kept in constant motion. These grow through the deposition of nickel; the metal obtained in this way is quite free from cobalt, but contains about 0.25 per cent of iron owing to the simultaneous formation of iron carbonyl.

In 1891 Berthelot and—simultaneously—Mond and Quincke³ found that reduced iron also absorbed carbon monoxide, forming an iron carbonyl $\text{Fe}(\text{CO})_5$. Whereas, however, active nickel, obtained by reducing the oxide or oxalate at temperatures below 300° , absorbs carbon monoxide avidly, iron is less reactive. According to Mittasch,⁴ the reactivity is very sensitive to traces of impurity in the gas or metal; pure iron is as reactive as nickel, and whereas traces of oxygen inhibit the reaction, traces of sulphur promote it strongly. Since the reaction is attended by a large decrease in volume, the formation of metal carbonyls is promoted by working at elevated pressures. At high pressures, indeed, the action of carbon monoxide is pronounced, even upon massive iron, so that iron carbonyl is invariably formed in gas cylinders containing compressed carbon monoxide or gases containing carbon monoxide (*e.g.* technical hydrogen). Iron pentacarbonyl is now produced technically on a considerable scale from iron, reduced from ferric oxide in hydrogen at 500° , and carbon monoxide at $180-200^{\circ}$ and 50–200 atmospheres pressure. Under similar conditions, and especially in the presence of sulphur as a promoter, cobalt, molybdenum and tungsten have also been converted into their carbonyls on a technical scale.

Iron pentacarbonyl was formerly used in antiknocks, but its chief technical importance is as a source of very pure iron. The decomposition of iron carbonyl on hot surfaces tends to give an inhomogeneous and carburized product, but decomposition in the vapour phase—*e.g.* by injecting the vapour into a space heated by radiant heat to $200-250^{\circ}$ —gives an extremely finely divided iron, known as 'carbonyl iron', which is quite pure except for a small

³ M. Berthelot, *Compt. rend.*, 1891, 112, 1343; L. Mond and F. Quincke, *J.C.S.*, 1891, 59, 604.

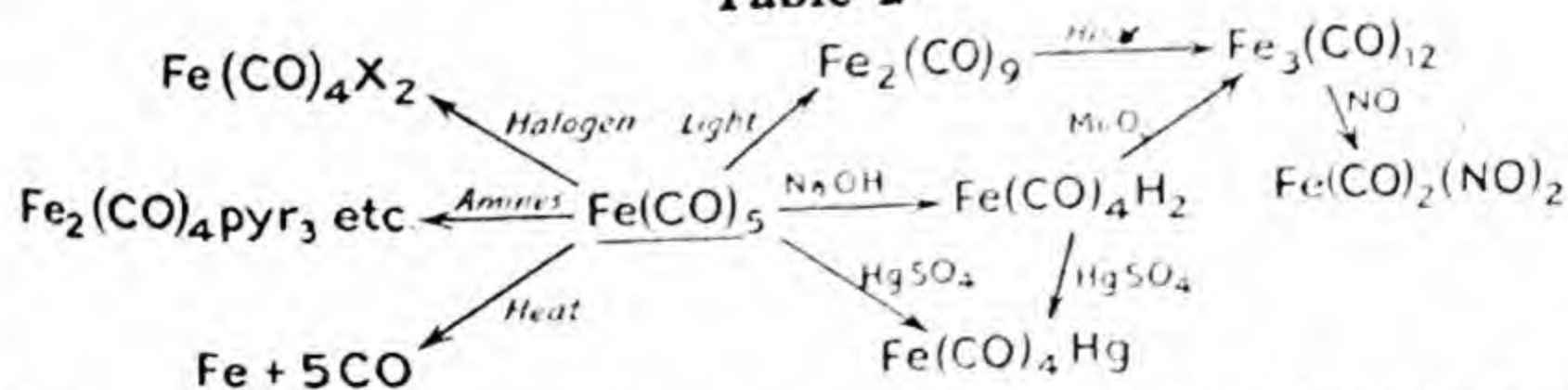
⁴ *Angew. Chem.*, 1928, 41, 827.

proportion of oxide and free carbon. The finely divided material is particularly suited for magnet cores and catalytic purposes. The small amount of impurity may be almost completely removed by fusing the iron in an induction furnace with the requisite amount of pure ferric oxide (also obtained by the oxidation of iron carbonyl). By this means, the carbon may be reduced below 0.0007 per cent, and the oxygen below 0.01 per cent.

Chemical Reactions of the Metal Carbonyls.—The variety of chemical reactions undergone by the carbonyls gives them a peculiar interest. They are highly reactive, and give rise to a number of quite new classes of metallic compounds. Nevertheless, until recent researches—notably those of Hieber and his co-workers—the only recorded reactions of the carbonyls were their decompositions by a variety of reagents—halogens, oxidizing agents, etc. Early workers failed to appreciate the extreme sensitiveness of the intermediate compounds, especially towards oxidation. Only by applying an experimental technique which was first worked out by Schlenk, for the manipulation of the highly reactive organic free radicals in a dry atmosphere completely free from oxygen, has it been possible to elucidate the chemistry of the metal carbonyls. Thus it is notable that Dewar and Jones observed that the green solution of iron tetracarbonyl in pyridine rapidly turned red, becoming finally colourless only when the iron was completely oxidized by the air. They do not, however, seem to have drawn the obvious inference that the colour change implied some intermediate reaction. In the recent work on the carbonyls, iron carbonyl has filled a special role, owing to the diversity of its reactions; this reactivity may be largely attributed to the fact that in $\text{Fe}(\text{CO})_5$, and also, probably, in the condensed carbonyls $\text{Fe}_2(\text{CO})_9$ and $\text{Fe}_3(\text{CO})_{12}$, the iron has a co-ordination number of five, and so is co-ordinatively unsaturated.

Some typical reactions of iron pentacarbonyl are briefly summarized in Table 2 below.

Table 2



The principal types of derivatives are indicated in Table 2, and are discussed in this chapter. The carbonyls themselves, and the amine substituted carbonyls, raise some interesting structural

problems, since they appear to belong to the class of purely 'secondary valency' compounds. The nitrosyl carbonyls link the chemistry of the metal carbonyls with that of the longer-known nitrosyl complexes of iron, ruthenium and other metals, just as the carbonyl halides of iron, etc., can be correlated with the well-established co-ordination chemistry of the platinum metals. In the subsequent sections of this chapter, emphasis is laid especially on the role of mixed valence type compounds, such as the carbonyl halides, in the direct synthesis of the carbonyls, and on the disproportionation processes involved in indirect syntheses.

Metal Carbonyl Halides.—With the exception of the Group VI metals, the elements which form carbonyls form carbonyl halides also (Table 3). In addition, such compounds are formed by palladium, platinum and the coinage metals. It is likely that

Table 3

Metallic Carbonyl Halides and Related Compounds

Mn —	Fe(CO) ₅ X ₂ Fe(CO) ₄ X ₂ [Fe(CO) ₃ Br ₂] ₃ Fe(CO) ₂ X ₂ Fe(CO) ₂ I K ₃ [Fe(ON) ₅ CO]	Co(CO)I ₂	Ni —	Cu(CO)X
		K ₃ [Co(CN) ₅ CO]	K ₂ [Ni(CN) ₃ CO]	
	Ru(CO) ₂ X ₂ Ru(CO)Br	[Rh(CO) ₂ X] ₂	[Pd(CO)Cl ₂] _n H[Pd(CO)Cl ₃]	Ag ₂ SO ₄ .CO
Re(CO) ₅ X	Os(CO) ₄ X ₂ Os(CO) ₃ X ₂ Os(CO) ₂ X ₂ [Os(CO) ₄ X] ₂	Ir(CO) ₃ X Ir(CO) ₂ X ₂	Pt(CO) ₂ Cl ₂ [Pt(CO)X ₂] ₂ H[Pt(CO)X ₃]	Au(CO)Cl

other compounds of this class may be discovered, for the cobalt compound Co(CO)I₂ has only recently been isolated.⁵ There is only indirect evidence for the existence of analogous nickel compounds, although the complex cyanide K₂[Ni(CN)₃CO] is well established.⁶ It is noteworthy that for the metals Pd, Pt, Cu, Au, which form no carbonyls, the carbonyl halides decrease in stability in the order chloride > bromide > iodide, whereas with the metals that form carbonyls both the stability and the volatility trend in the converse direction.

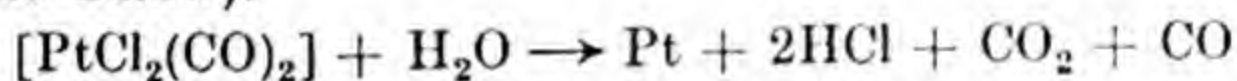
⁵ H. Schulten, *Z. anorg. Chem.*, 1939, **243**, 145.

⁶ W. Manchot and H. Gall, *Ber.*, 1926, **59**, 1060.

The most general mode of formation of metal carbonyl halides is by direct combination of carbon monoxide with anhydrous metallic halides. Thus Schützenberger⁷ discovered in 1869 that spongy platinum reacted at 250° with a mixture of carbon monoxide and chlorine, forming a pale yellow crystalline sublimate, from which he isolated $\text{PtCl}_2\cdot\text{CO}$, $\text{PtCl}_2(\text{CO})_2$ and $2\text{PtCl}_2\cdot 3\text{CO}$. The same compounds are formed by the action of carbon monoxide on the chlorides of platinum. The yellow $\text{PtCl}_2\cdot\text{CO}$ is obtained in the pure state by thermal decomposition of the higher carbonyl chlorides; it decomposes only above 300°, but reacts with carbon monoxide at 150°, forming $\text{PtCl}_2(\text{CO})_2$. This is monomeric, and a non-electrolyte; by analogy with other co-ordination compounds of the type $\text{PtCl}_2\cdot\text{X}$, the monocarbonyl chloride is probably dimeric (*cf.* Chap. VI, p. 153). Both compounds, dissolved in carbon tetrachloride, react with ammonia forming amines which may probably be regarded as the salts $[\text{Pt}(\text{CO})_2(\text{NH}_3)_2]\text{Cl}_2$ and $[\text{PtCl}(\text{CO})(\text{NH}_3)_2]\text{Cl}$ respectively. Carbon monoxide is displaced from the carbonyl halides by the action of phosphorus trichloride, but not by amines:



All these compounds are very sensitive towards water, with which they react in a manner completely different from iron carbonyl halides (*see below*).



They dissolve unchanged in hydrochloric acid, owing to the formation of the complex acid $\text{H}[\text{PtCl}_3\cdot\text{CO}]$, which may be isolated in the form of its salts, which, like the parent carbonyl chlorides, are decomposed by water.

With hydrobromic and hydriodic acids, the corresponding carbonyl bromide and iodide are formed.⁸ These have a lower thermal stability, but an increased stability towards chemical decomposition—*e.g.* by water.

PtCl_2CO	PtBr_2CO	PtI_2CO
yellow.	orange-red.	red.
Volatile without decomposition, m.p. 195°.	Difficultly volatile, m.p. 181°.	Non-volatile and decomposed on heating, m.p. 140°.
Hygroscopic, immediately decomposed by water	Hygroscopic and decomposed by water	Not readily decomposed by water

The behaviour of palladium is worthy of notice as coming between nickel, of which no carbonyl halides are known, and

⁷ *Ann. Chim.*, 1871, **15**, 100; **21**, 250.

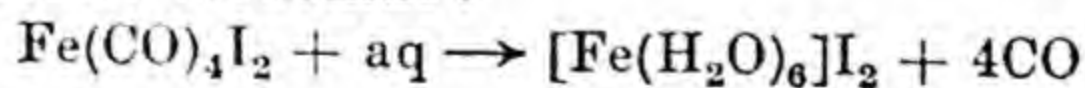
⁸ F. Mylius and F. Foerster, *Ber.*, 1891, **24**, 2424, 3751.

platinum, which forms the compounds just considered. Palladous chloride forms the one compound $\text{PdCl}_2 \cdot \text{CO}$ by the action of carbon monoxide at the ordinary temperature (in presence of methyl alcohol vapour as catalyst),⁹ but is without action on carbon monoxide at elevated temperatures. Palladous carbonyl chloride is rather less sensitive towards water than are the platinum compounds, but the carbon monoxide is only loosely bound, being displaced quantitatively by hydrobromic or hydriodic acids. Like the platinum compound, it dissolves in hydrochloric acid, forming $\text{H}[\text{PdCl}_3 \cdot \text{CO}]$; salts of this acid are extremely readily decomposed by water.

Compounds of generally similar properties have been described as formed from the chlorides of gold,¹⁰ iridium¹¹ and osmium.¹² Little is known of their chemistry, except in so far as it has entered into recent studies of the platinum metal carbonyls proper. Table 3 brings together all these compounds, for comparison with the carbonyl halides formed by the metals of the first transition series. There is an evident tendency to form compounds which permit of the attainment of the stable co-ordination numbers 6 and 4 (probably square planar configuration), either in monomeric compounds—*e.g.* $[\text{Re}(\text{CO})_5\text{X}]$, $[\text{Os}(\text{CO})_4\text{X}_2]$, $[\text{Ir}(\text{CO})_3\text{X}]$ —or in binuclear complexes, as in $[\text{Os}(\text{CO})_3\text{X}_2]_2$, $[\text{Rh}(\text{CO})_2\text{X}]_2$.

Iron Carbonyl Halides.—By contrast with the carbonyl halides of platinum metals, iron carbonyl halides were discovered, and are best prepared, by the action of halogens on iron pentacarbonyl.¹³ The initial products of reaction are unstable addition compounds $\text{Fe}(\text{CO})_5\text{X}_2$, which decompose spontaneously, forming the tetracarbonyl halides, even at low temperatures (Table 4). These latter compounds are stable enough to be formed directly by the union of anhydrous ferrous halides with carbon monoxide under pressure.¹⁴ For $\text{Fe}(\text{CO})_4\text{I}_2$, the dissociation pressure is about 6 atmospheres at the ordinary temperature.

All these compounds are non-electrolytes, soluble in inert organic solvents. They are completely decomposed by water into ferrous halide and carbon monoxide:



⁹ W. Manchot and J. König, *ibid.*, 1926, 59, 883.

¹⁰ W. Manchot and H. Gall, *Ber.*, 1925, 58, 2175; M. S. Kharasch and H. S. Isbell, *J. Amer. Chem. Soc.*, 1930, 52, 2918.

¹¹ W. Manchot and H. Gall, *Ber.*, 1925, 58, 232.

¹² W. Manchot, *ibid.*, 1925, 58, 229.

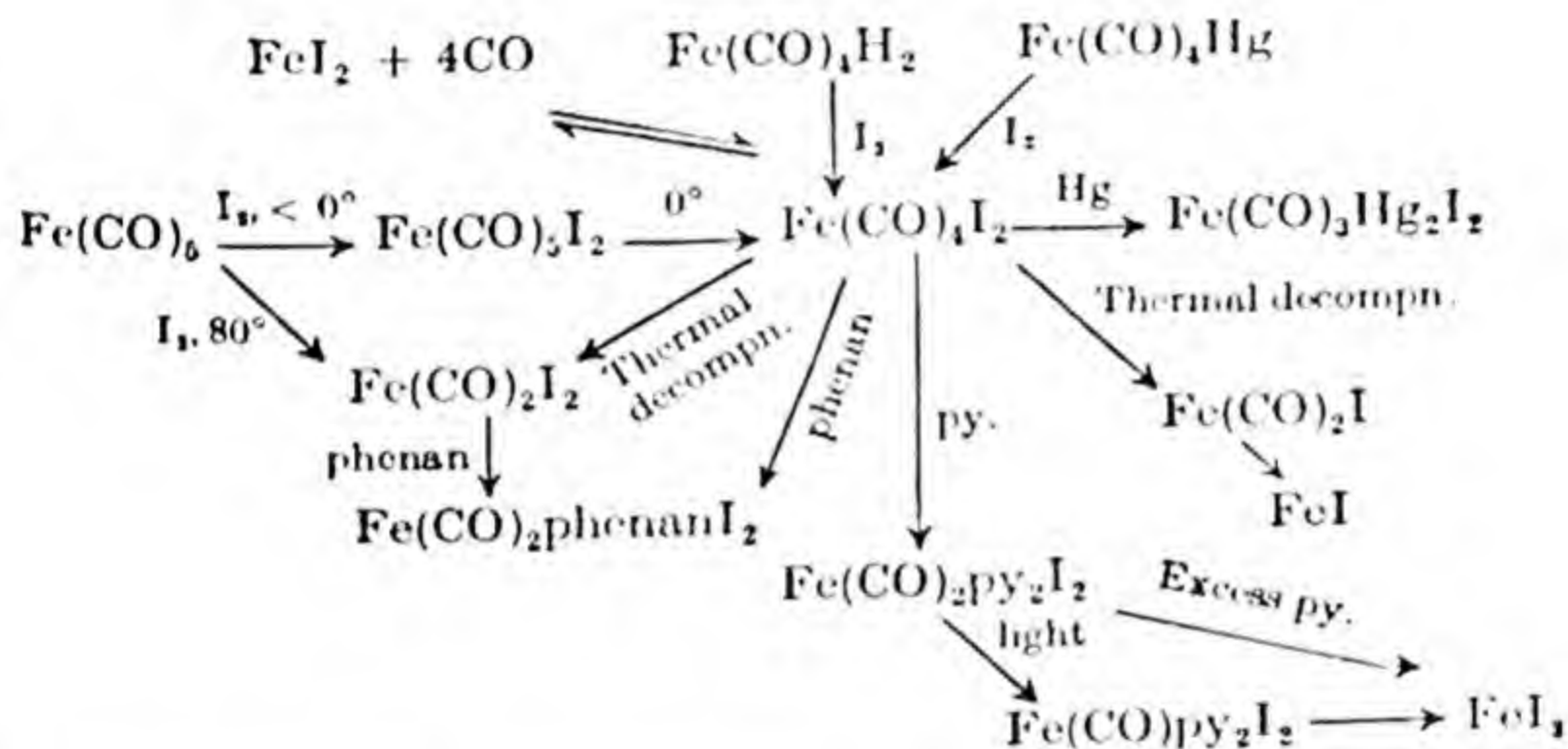
¹³ W. Hieber and G. Bader, *Ber.*, 1928, 61, 1717; *Z. anorg. Chem.*, 1931, 190, 193; 201, 329.

¹⁴ W. Hieber, *Z. Elektrochem.*, 1937, 43, 390; W. Hieber and H. Lagally, *Z. anorg. Chem.*, 1940, 245, 305.

An essentially similar decomposition is effected by pyridine and other amines in excess, but with these the displacement of carbon monoxide may proceed in stages. As the CO groups are progressively replaced by pyridine, phenanthroline, etc., the thermal stability of the compounds is raised.

The formation of $\text{Fe}(\text{CO})_4\text{I}_2$ from ferrous iodide and carbon monoxide is reversible: although the compound may be sublimed in vacuum, it is decomposed by heating. A number of intermediate products have been identified in this process,¹⁵ including the lower carbonyl iodide $\text{Fe}(\text{CO})_2\text{I}_2$ and a derivative of univalent iron, partially stabilized by co-ordination of CO groups, $\text{Fe}(\text{CO})_2\text{I}$. In the thermal decomposition of this latter compound it is said that the very unstable red FeI is formed. All these types of reactions are schematically brought together in Table 4.

Table 4

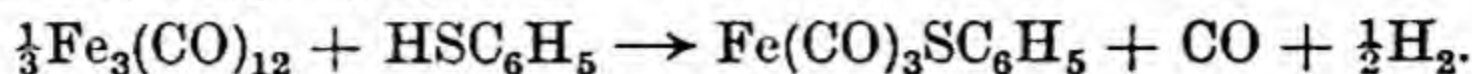


Iron Carbonyl Thio-compounds.—Other negative atoms or groups may enter iron carbonyl, forming compounds which are analogous to the carbonyl halides. Of these, the compounds formed in reactions of iron carbonyls (especially $\text{Fe}_3(\text{CO})_{12}$) with organic sulphur compounds are of some interest, being indicative of possible intermediates in the synthetic reactions shortly to be considered. Moreover, they link the chemistry of iron carbonyl with that of the nitrosyl thio-compounds of iron, long known under the names of the red and black salts of Roussin.¹⁶

¹⁵ W. Hieber and H. Lagally, *Z. anorg. Chem.*, 1940, 245, 295.

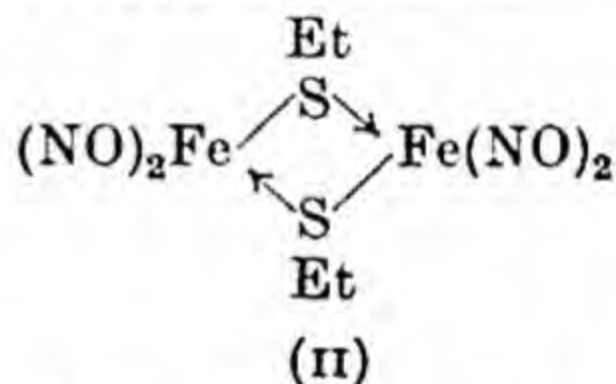
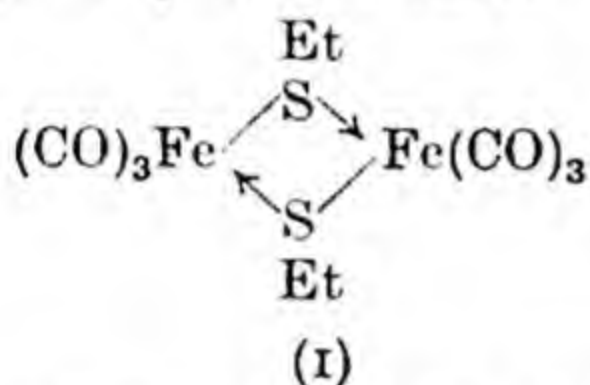
¹⁶ Hofmann and Wiede, *Z. anorg. Chem.*, 1895, 9, 295; Gmelin-Kraut, *Iron*, B, pp. 471-7; Manchot, *Ber.*, 1926, 59, 2445; 1927, 60, 2175; 1928, 61, 2393; 1929, 62, 681; *Annalen*, 1927, 459, 47; 1928, 465, 304; 1929, 470, 255, 261.

Thiophenol yields with iron tetracarbonyl the tricarbonyl mercaptide $\text{Fe}(\text{CO})_3\text{SC}_6\text{H}_5$:

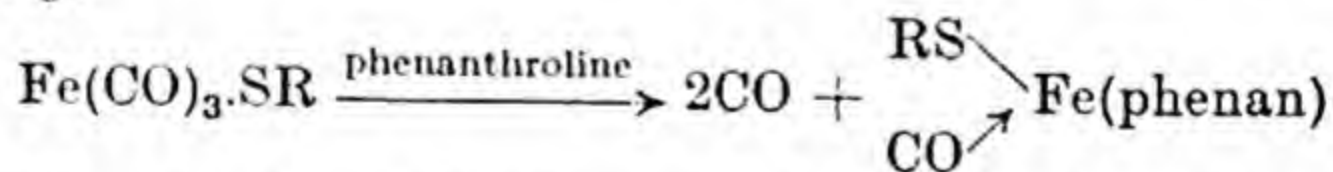


This compound, which is monomeric in organic solvents, is remarkably stable.¹⁷ Unlike most carbonyl compounds, it is unaffected by atmospheric oxygen, and does not react with nitric oxide; even concentrated sulphuric acid or alkaline perhydrol has no action upon it. It is decomposed by hydrogen chloride at $100\text{--}140^\circ$, forming ferrous chloride. From cobalt tetracarbonyl a similar compound, $\text{Co}(\text{CO})_3\text{SC}_6\text{H}_5$, is obtained.

Other mercaptans react similarly, but the analogous ethyl mercaptides are dimeric in solution (I). Beside these compounds may be placed the esters of Roussin's red salts—*e.g.* $\text{Fe}_2(\text{NO})_4(\text{SEt})_2$ (II). It may be seen that the two classes of compound are related in exactly the same way as are $\text{Fe}(\text{CO})_5$ and $\text{Fe}(\text{CO})_2(\text{NO})_2$, or $\text{Fe}(\text{CO})_3\text{phth}$ and $\text{Fe}(\text{NO})_2\text{phth}$, two molecules of nitric oxide taking the place of three molecules of carbon monoxide.



As accords with their stability, the carbonyl mercaptides cannot be converted to Roussin's salts. Organic disulphides, such as $\text{C}_6\text{H}_5\text{.S.S.C}_6\text{H}_5$, behave as pseudo-halogens; the —S—S— bond breaks, and the same compounds result as with thiophenols.¹⁸ As in the carbonyl halides, CO groups may be partially displaced by amines—*e.g.*



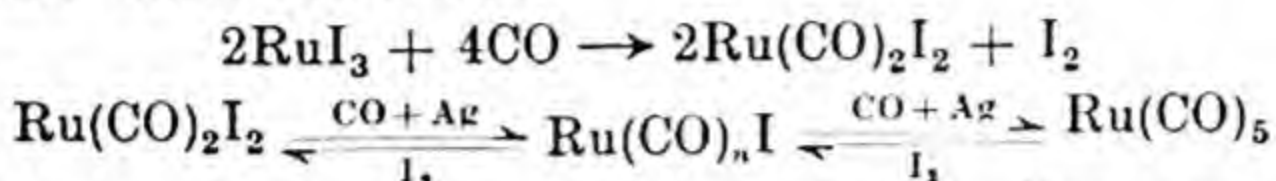
Carbonyls of the Platinum Metals.—The data given in Table 1 show a very close resemblance in each of the vertical series Fe—Ru—Os and Co—Rh—Ir , as regards the formation of carbonyls and their derivatives. There is, however, a marked difference in reactivity within these groups. Whilst rhodium is reactive enough to combine with carbon monoxide under pressure, osmium and iridium are completely unreactive; the carbonyls of all these metals have been prepared from the halides of the metals.

The possibility of reactions of this kind was demonstrated by

¹⁷ W. Hieber and G. Spacu, *Z. anorg. Chem.*, 1937, **233**, 353.

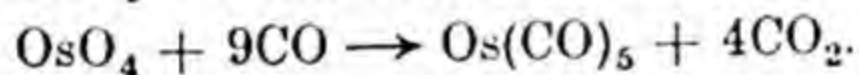
¹⁸ W. Hieber and C. Scharfenberg, *Ber.*, 1940, **73**, 1012.

W. Manchot and W. J. Manchot¹⁹ in their preparation of ruthenium pentacarbonyl, $\text{Ru}(\text{CO})_5$. Ruthenium iodide, RuI_3 , reacts with carbon monoxide even at the ordinary pressure, forming the carbonyl iodide $\text{Ru}(\text{CO})_2\text{I}_2$. In the presence of an *acceptor for halogen*, such as finely divided silver, not only does this reaction go to completion at 170° , but the displacement of halogen can proceed further, and ruthenium pentacarbonyl is formed. A number of successive reversible reactions are displaced completely towards the right under these conditions:



Although the reaction takes place also at the ordinary pressure, the pentacarbonyl is best prepared by heating RuI_3 with carbon monoxide and silver under pressure (*e.g.* at 170° and 250 atm.). The similarity between iron and ruthenium carbonyls is close. Ruthenium pentacarbonyl, like that of iron, is photosensitive, losing half a molecule of CO and forming $\text{Ru}_2(\text{CO})_9$, which (unlike $\text{Fe}_2(\text{CO})_9$) is also formed by heating $\text{Ru}(\text{CO})_5$ at 50° .

The osmium carbonyls $\text{Os}(\text{CO})_5$ and $\text{Os}_2(\text{CO})_9$ have been prepared in a similar manner from the osmium halides.²⁰ The carbonyl halides are intermediates in the process, and the mere presence of a copper or silver lining in the autoclave serves to bind the halogens. In this case the successive steps in the reaction may be demonstrated experimentally, for $[\text{Os}(\text{CO})_4\text{I}_2]$, first formed, reacts at 120° with silver powder, forming $[\text{Os}(\text{CO})_4\text{I}]_2$. Osmium carbonyl is even more readily formed by an unusual reaction, from osmium tetroxide.



Some kind of carbonyl oxide is presumably formed in this process, although compounds of this class have not been isolated.

The rhodium carbonyls²¹ $[\text{Rh}(\text{CO})_4]_2$, $[\text{Rh}(\text{CO})_3]_x$ and $[\text{Rh}_4(\text{CO})_{11}]_y$ and iridium carbonyls²² $[\text{Ir}(\text{CO})_4]_2$ and $[\text{Ir}(\text{CO})_3]_x$ bear a formal resemblance to the cobalt compounds, but little is as yet known of their chemical properties. They are prepared by methods similar to those already discussed.

The compounds listed in Table 1 suggest that, between the hexacarbonyls $[\text{M}(\text{CO})_6]$ of the Group VI metals and the pentacarbonyls $[\text{M}(\text{CO})_5]$ and tetracarbonyl halides $[\text{M}(\text{CO})_4\text{I}_2]$ of the iron-ruthenium-osmium family, one might expect to find dimeric

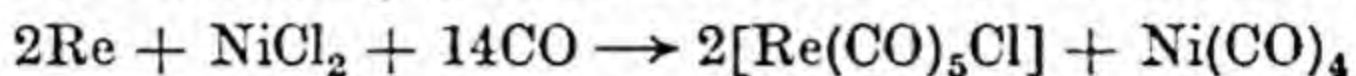
¹⁹ *Z. anorg. Chem.*, 1936, 226, 385.

²⁰ Hieber and H. Stallmann, *Z. Elektrochem.*, 1943, 49, 288; *Ber.*, 1942, 75, 1472; *cf.* also W. Manchot and J. König, *ibid.*, 1925, 58, 229.

²¹ *Z. anorg. Chem.*, 1943, 251, 96.

²² *Ibid.*, 1940, 245, 321.

pentacarbonyls $[M(CO)_5]_2$ and pentacarbonyl halides $[M(CO)_5X]$ formed by the metals of Group VII. Manganese, in accordance with its tendency to differ from the other elements, appears to form no carbonyl. Rhenium, however, forms compounds with the predicted composition and properties.²³ The rhenium carbonyl halides $[Re(CO)_5X]$ are, in fact, so stable that they are invariably formed from halogen compounds of rhenium—*e.g.* $ReCl_5$, $K_2[ReBr_6]$, etc.—in the high pressure synthesis. The iodide is formed when $K_2[ReI_6]$ is heated in carbon monoxide even at the ordinary pressure, and in the presence of carbon monoxide metallic rhenium can even abstract halogen from the halides of the transition metals:



In the case of rhenium, the carbonyl halides are so stable that they cannot be converted into rhenium carbonyl itself by any known reaction. The carbonyl is obtained, instead, by the action of carbon monoxide on the oxides and oxysalts— Re_2O_7 or $KReO_4$ —or sulphide Re_2S_7 .

The dimeric carbonyl, $(CO)_4Re \overset{CO}{\underset{CO}{\parallel}} Re(CO)_4$, resembles in its stability and inertness the hexacarbonyls of chromium and its congeners, which are co-ordinatively saturated. It is decomposed neither by alkalis nor concentrated mineral acids, and although not very volatile, can be sublimed in carbon monoxide at 200° . Its reactions resemble those of iron pentacarbonyl, in that with gaseous halogens it forms the stable carbonyl halides, whilst amines such as pyridine or phenanthroline effect a partial displacement of carbon monoxide.

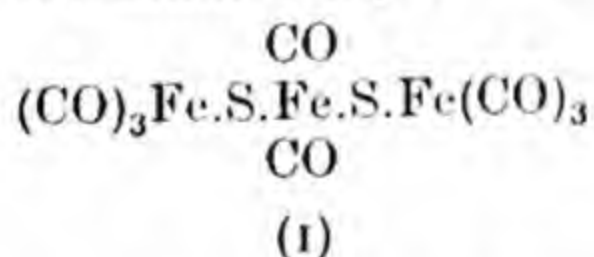
The part played by the carbonyl halides in the synthesis of the platinum metal carbonyls suggests that analogous reactions might take place with the metals of the iron group, especially as there are several references in patent specifications to the catalytic effect of iodine and sulphur in the formation of metal carbonyls. With the iron group metals, which form compounds of true ionic type, not all compounds lend themselves, however, to the high pressure carbonyl synthesis. Thus CoF_2 (rutile structure) and CoO (rock salt structure) form no cobalt carbonyl, whereas the sulphide (nickel arsenide structure) or the iodide (cadmium iodide layer lattice structure) give cobalt carbonyl in substantial yield.²⁴ The reaction is thus effective with the compounds of highly polarizable non-metals, capable of forming carbonyl halides, etc., of essentially

²³ W. Hieber and H. Schulten, *Z. anorg. Chem.*, 1939, **243**, 164; W. Hieber, R. Schuh and H. Fuchs, *ibid.*, 1941, **248**, 243, 256.

²⁴ W. Hieber, H. Schulten and R. Marin, *Z. anorg. Chem.*, 1939, **240**, 261.

homopolar type. From cobalt iodide, a quantitative yield of cobalt carbonyl is obtained even when there is no direct contact with the silver or copper lining of the autoclave, pointing to the existence of a volatile cobalt carbonyl iodide as an intermediate. This intermediate compound has been isolated by Schulten,²⁵ who found that $\text{Co}(\text{CO})\text{I}_2$ was formed as a dark brown crystalline solid at the ordinary temperature, under a high pressure of carbon monoxide. The halides of iron and nickel react similarly, except that $\text{Fe}(\text{CO})_4\text{I}_2$ is so stable that its ultimate conversion to iron pentacarbonyl remains very incomplete.

From all this work we may gain some insight into the mechanism whereby metals react with carbon monoxide. In the direct reaction, carbon monoxide must first be chemisorbed, but if the surface is readily poisoned (as, for example, by traces of oxygen), or if the carbonyl itself is too strongly adsorbed, the reaction is practically inhibited. Elements like iodine can play a catalytic role by entering into a cyclic set of reactions whereby the metallic iodide is formed, converted at each stage into the carbonyl iodide, and thence into carbonyl and fresh metallic iodide. Sulphur undoubtedly undergoes a similar catalytic cycle in technical carbonyl processes. It has, indeed, been possible to isolate a violet-red, well-crystallized iron carbonyl sulphide,²⁶ $\text{Fe}_3\text{S}_2(\text{CO})_8$ —probably formulated as (I)—by the combined action of carbon monoxide and hydrogen sulphide upon iron. A similar selenium compound has been prepared also.



In the catalytic action of sulphur and selenium, the cycle of catalytic reactions takes place upon the surface of the metal. The formation of the intermediate compounds in bulk is not necessary, and the optimum conditions are, indeed, obtained when the quantity of sulphur present is relatively small.

The Indirect Formation of Metal Carbonyls.—The carbonyls of the iron triad and of the Group VI metals can be prepared by reactions quite different from those just considered. The feature common to these processes, which take place in aqueous or non-aqueous solution, is the occurrence of a disproportionation reaction in which some unstable compound, a co-ordination compound derived from a lower valence state of the metals, disproportionates

²⁵ *Ibid.*, 1939, 243, 145.

²⁶ W. Hieber, in FIAT Review of German Science, 1939–46, Inorganic Chemistry, Part II, p. 116.

into a stable compound of a higher valence state and the effectively zero-valent state present in the metal carbonyl.

The first reaction which may be noted is the preparation of carbonyls in non-aqueous solvents by a Grignard reaction. This provides the only practicable laboratory preparation of the hexacarbonyls of chromium, molybdenum and tungsten, even though R. L. Mond, by careful reduction of molybdenum oxychloride, obtained a metal which was sufficiently active to combine slowly with carbon monoxide at high pressures, and to show the existence of molybdenum carbonyl. Job, in 1926, found that the slow reaction between carbon monoxide and the Grignard reagent was accelerated by salts of the transition metals, and particularly by anhydrous chromic chloride. The organic products of this reaction are complex, but an ether-soluble compound of chromium could be isolated in small yield; this proved to be chromium carbonyl, $\text{Cr}(\text{CO})_6$. A. Job and J. Rouvillois²⁷ subsequently prepared tungsten hexacarbonyl, $\text{W}(\text{CO})_6$, in the same way from tungsten hexachloride.

The mechanism of this process has not yet been worked out, but the key to its interpretation is probably to be found in Hein's work on the chromphenyl compounds²⁸—the organometallic compounds which are formed by the action of phenyl magnesium bromide on chromic chloride. This work has shown that, in addition to the organo-chromium halides derived from pentavalent chromium, the chromic chloride disproportionates, forming chromous chloride and also a compound of apparently univalent chromium. Hieber and Romberg²⁹ have shown that no chromium carbonyl is formed until the last stage of the reaction, when the Grignard addition products are hydrolysed. The initial reaction of the carbon monoxide must presumably be to form some addition compound with the supposed univalent chromium, or with chromium aryls—*e.g.* such a compound as $\text{Cr}(\text{CO})_2\text{R}_4$, suggested by Hieber. This forms chromic ion and $\text{Cr}(\text{CO})_6$ amongst other products when it is decomposed by acid:

$$3\text{Cr}(\text{CO})_2\text{R}_4 + 6\text{H}^+ \rightarrow \text{Cr}(\text{CO})_6 + \text{Cr}^{3+} + 12\text{R} + 6\text{H} \rightarrow$$

organic products.

Hieber's mechanism is hypothetical, for no intermediate compounds have been characterized; dismutation processes of the kind involved

²⁷ *Compt. rend.*, 1926, 183, 392; 1928, 187, 564; *Bull. Soc. Chim.*, 1927, 41, 1041.

²⁸ *Ber.*, 1921, 54, 1905, 2708; 1924, 57, 8, 899; 1926, 59, 362, 751; 1927, 60, 679, 749, 2388; 1928, 61, 730, 2255; 1929, 62, 1151. A résumé is given in *J. prakt. Chem.*, 1931, 132, 59. See also Klemm and Neuber, *Z. anorg. Chem.*, 1936, 227, 261.

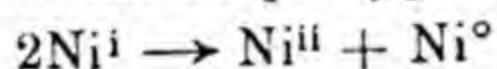
²⁹ *Z. anorg. Chem.*, 1935, 221, 321.

are, however, commonly observed in the acid decomposition of substituted carbonyls.

Only the non-polar halides (CrCl_3 , MoCl_5 , WCl_6) enter into the Grignard reaction. Stable complex salts do not react, even though they may be non-electrolytes; the metal atom may, perhaps, be blocked from some initial step of co-ordination with carbon monoxide. The existence of organometallic compounds of molybdenum and tungsten, comparable with the chromophenyls, is rather uncertain.³⁰

The hexacarbonyls of Group VI metals are colourless, crystalline solids, much more stable than iron pentacarbonyl or nickel carbonyl. They are not oxidized in air, and may be sublimed without decomposition. The deposition of chromium from chromium carbonyl is perceptible only at temperatures above 140° . The same stability is shown towards chemical attack. Chromium carbonyl is unaffected by bromine, although it is decomposed by chlorine or nitric acid. The molybdenum compound is less resistant, but is nevertheless more stable than are the carbonyls of the iron group.

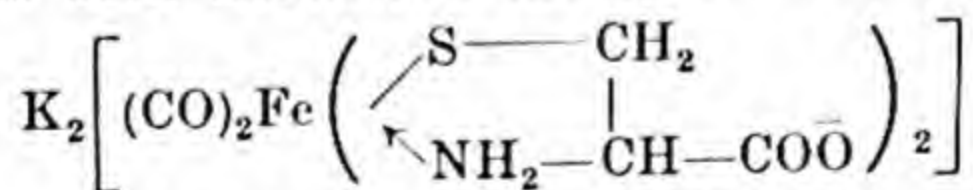
Formation of Nickel Carbonyl in Aqueous Solutions.—The disproportionation involved at some stage of Job's Grignard synthesis has its parallel in the formation of nickel carbonyl from complex compounds of carbon monoxide. These processes hinge on the displacement of oxidation-reduction potentials in the complex salt systems and involve the steps typified by



or



Similar processes leading to the formation of iron pentacarbonyl have not been observed. Whilst the ferrous salts of a few organic thio-acids do absorb carbon monoxide (up to 2 mols per atom of Fe^{II} , in the case of the xanthate), the only carbonyl addition compound that has been isolated is the cysteine complex,



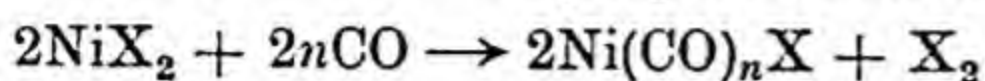
Cobalt salts react like those of nickel, but form the monomeric cobalt carbonyl hydride in place of the dimeric cobalt carbonyl. This latter reaction is mentioned in a later section.

W. Manchot and H. Gall³¹ first observed that nickel sulphide or cyanide suspended in caustic soda solution would absorb carbon

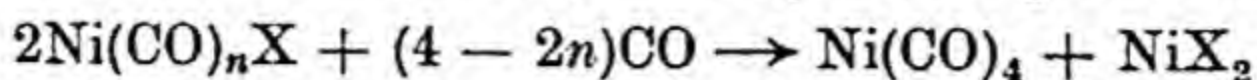
³⁰ Cf. F. Hein, *Angew. Chem.*, 1936, 49, 761; *J. prakt. Chem.*, 1939, 153, 160.

³¹ W. Manchot and H. Gall, *Ber.*, 1929, 62, 678; also A. A. Blanchard, J. R. Rafter and W. B. Adams, *J. Amer. Chem. Soc.*, 1934, 56, 16.

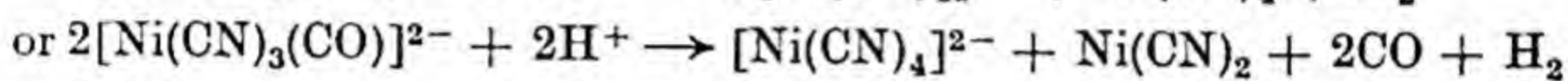
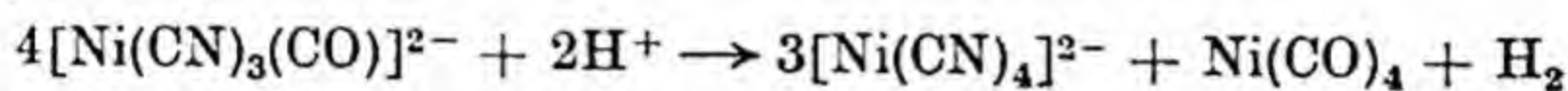
monoxide, forming nickel carbonyl. They suggested that the initial step was to form a carbonyl complex of univalent nickel, which in turn underwent disproportionation :



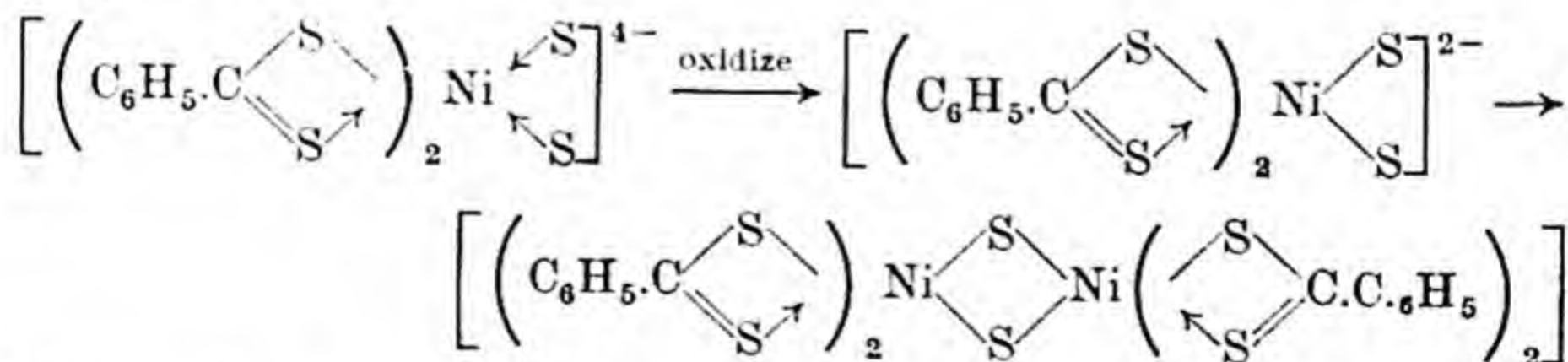
(X = —CN, —SH, —SCH₃, etc., X₂ absorbed by alkali)



In accordance with this scheme, the complex cyanide of univalent nickel first prepared by Belucci,³² K₂[Ni(CN)₃], absorbs carbon monoxide, forming the 4-co-ordinated complex K₂[Ni(CN)₃(CO)].³³ This can be isolated from liquid ammonia solutions, but in water it reacts too readily with hydrogen ions, according to either of the equations



Sulphur compounds play a remarkably specific part in reactions of this kind. The nickel salts of organic thio-acids—xanthate, thiosalicylate, thioacetate, thioglycollate, etc.—all absorb carbon monoxide in alkaline solutions, and react as shown above. So also do the nickel ammine salts of certain inorganic thio-acids, such as [Ni(NH₃)₆][MoS₄]. As a rule, the absorption of carbon monoxide amounts to 2 molecules per atom of nickel, while only half of the nickel entering into the reaction is ultimately recoverable as nickel carbonyl. It has been shown by Hieber and Brück³⁴ that in certain cases, at least, the reactions occur because the thio-compounds so stabilize the existence of compounds of quadrivalent nickel that they are formed from bivalent nickel compounds even by atmospheric oxygen (cf. Chap. VI, p. 180). Thus, nickel (ii) thiobenzoate forms with sulphide ion a complex thio-anion, of co-ordination number 6, which oxidizes readily to a nickel (iv) compound :



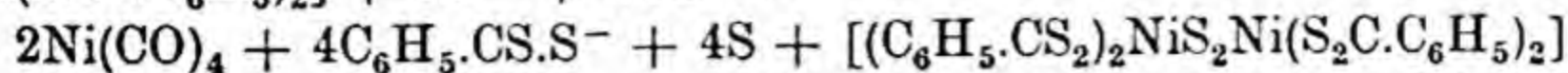
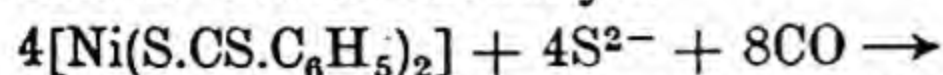
With carbon monoxide in place of an oxidizing agent, dispropor-

³² Z. anorg. Chem., 1914, 86, 88.

³³ W. Manchot and H. Gall, Ber., 1926, 59, 1060.

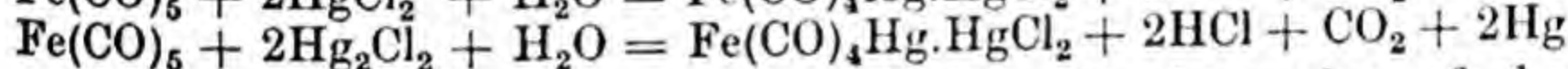
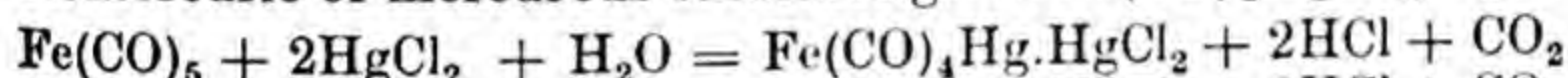
³⁴ Naturwiss., 1949, 36, 312.

tionation converts half of the nickel to this Ni (iv) complex, and half to nickel carbonyl:



Reactions of this type are not confined to thio-complexes. Nickel dimethylglyoxime disproportionates similarly in the presence of carbon monoxide, but in this case the nickel (iv) compound is unstable, and is reduced by carbon monoxide. All the nickel should thus be available for conversion to nickel carbonyl, and yields of 90 per cent are actually obtainable.

Iron and Cobalt Carbonyl Hydrides.—Hock and Stuhlmann³⁵ found that iron pentacarbonyl reacted with solutions of mercuric salts, forming very stable insoluble substitution products containing mercury, with the simultaneous liberation of one molecule of carbon dioxide. With one molecular proportion of mercuric sulphate, the compound $\text{Fe}(\text{CO})_4\text{Hg}$ is first formed, and this may be combined with a further molecule of mercuric salt, forming compounds of the type $\text{Fe}(\text{CO})_4\text{Hg.HgX}_2$. Thus, the action of iron pentacarbonyl on mercuric or mercurous chlorides gives $\text{Fe}(\text{CO})_4\text{Hg.HgCl}_2$ directly:



At low temperatures, in acetone solution, the formation of the intermediate compound $\text{Fe}(\text{CO})_5.\text{HgCl}_2$ may be detected. This undergoes decomposition at the ordinary temperature, or in presence of mercuric chloride, giving the above-mentioned products.

Mercury iron tetracarbonyl, $\text{Fe}(\text{CO})_4\text{Hg}$, is a stable, yellow substance, unchanged in air but decomposed quantitatively at 150° into mercury, iron and carbon monoxide. It reacts with the halogens at room temperatures, forming mercuric halides and the iron carbonyl halides (*see below*):



In contradistinction to most carbonyl compounds, it is unaffected by boiling pyridine.

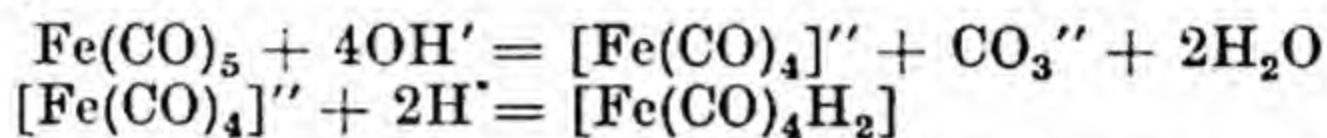
The exact nature of mercury iron tetracarbonyl was for some time in dispute. The tendency of mercury to form organo-metallic compounds suggested that the mercury might be joined covalently to carbon monoxide in some way. The evidence now shows that the substance is actually the mercuric derivative of the remarkable *iron carbonyl hydride*, $\text{Fe}(\text{CO})_4\text{H}_2$.

It had already been noticed, early in the study of the metal carbonyls,³⁶ that iron pentacarbonyl could be dissolved in alcoholic

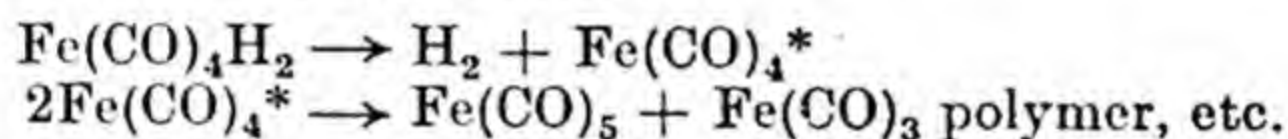
³⁵ *Ber.*, 1928, 61, 2097; 1929, 62, 431, 2690.

³⁶ *Proc. Roy. Soc.*, 1905, A, 76, 558; 1906, 79, 66.

potash, giving a solution which rapidly turned red in the air. Freundlich and Malchow³⁷ observed that the solution so obtained had strong reducing properties, and gave up to 40 per cent of iron tetracarbonyl on acidification. The latter is formed by atmospheric oxidation; by adding a mild oxidizing agent, such as manganese dioxide, the yield of iron tetracarbonyl may be raised to 90 per cent. Hieber found³⁸ that the action of bases—*e.g.* baryta—on iron pentacarbonyl was essentially one of hydrolysis, leading to the formation of carbonate, the amount of which approached one molecule per molecule of iron pentacarbonyl when a suitable excess of base was used. When the solutions resulting from the action of alkalis were acidified in the complete absence of oxygen, a new, volatile, very unstable compound of iron was liberated—iron carbonyl hydride.



Iron carbonyl hydride is a pale yellow, volatile liquid, m.p. -70° , with a characteristic, nauseating smell. It decomposes rapidly above -10° , giving free hydrogen and the products of decomposition of the Fe(CO)_4 radicle:



It has powerful reducing properties, and may be determined quantitatively by its decolorization of methylene blue. Like mercury iron tetracarbonyl, it reacts with iodine to give $\text{Fe(CO)}_4\text{I}_2$.

In aqueous solution, it has the properties of a weak (usually monobasic) acid. Thus Feigl and Krumholz³⁹ found that the salt $[\text{Fe(CO)}_4]\text{HNa}\cdot\text{CH}_3\text{OH}$ is formed in the hydrolysis of iron pentacarbonyl with sodium methoxide, whilst suspensions of calcium hydroxide and magnesia react to form $[\text{Fe(CO)}_4\text{H}]_2\text{Ca}$, $[\text{Fe(CO)}_4\text{H}]_2\text{Mg}$ respectively.⁴⁰ With the bulky metal aminocations,⁴¹ iron carbonyl hydride forms sparingly salts—*e.g.* the series $[\text{Fe(CO)}_4\text{H}]_2[\text{M}^{\text{II}}(\text{NH}_3)_6]$, where $\text{M}^{\text{II}} = \text{Mn, Fe, Co, or Ni}$, and $[\text{Fe(CO)}_4\text{H}]_2[\text{M}^{\text{II}}\text{phth}_3]$, where $\text{M}^{\text{II}} = \text{Co, Fe, Ni}$ and phth = ortho-phenanthroline. Salts of the latter type are very insoluble, and are precipitated quantitatively from solutions.

Iron carbonyl hydride differs from other classes of carbonyl derivatives in that it is not decomposed by pyridine and other

³⁷ *Ber.*, 1923, 56, 2264; *Z. anorg. Chem.*, 1924, 141, 317.

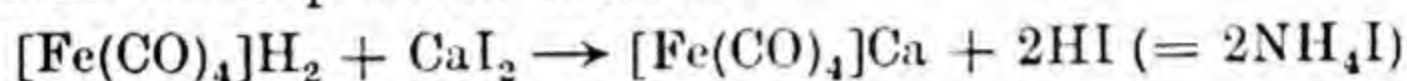
³⁸ *Ber.*, 1931, 64, 2832; *Z. anorg. Chem.*, 1931, 204, 145, 165.

³⁹ *Z. anorg. Chem.*, 1933, 215, 242.

⁴⁰ F. Hein and H. Poblth, *Z. anorg. Chem.*, 1941, 248, 84.

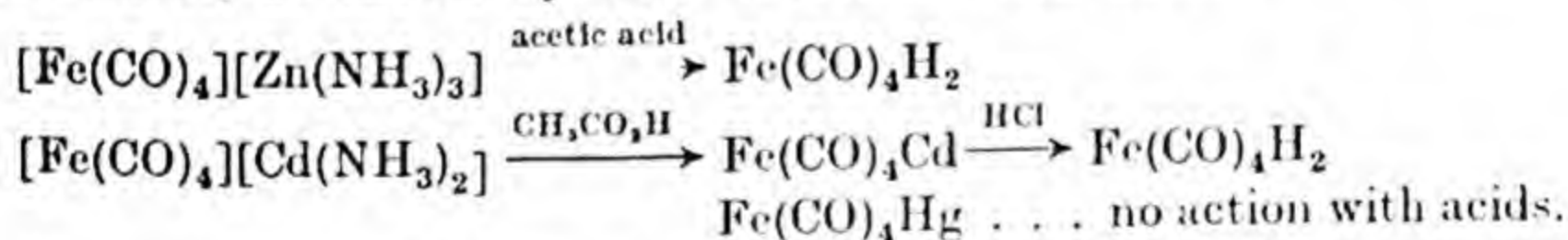
⁴¹ W. Hieber and H. Fack, *Z. anorg. Chem.*, 1938, 236, 83.

amines, but forms stable salts—*e.g.* $[\text{Fe}(\text{CO})_4](\text{C}_5\text{H}_5\text{N.H})_2$. Its solutions in pyridine and in liquid ammonia have the electrical conductivity of solutions of strong electrolytes, and from the liquid ammonia solutions it is possible to prepare the 'normal' salts of iron carbonyl hydride, by precipitation or evaporation—*e.g.* $[\text{Fe}(\text{CO})_4](\text{NH}_4)_2 \cdot 0.3\text{NH}_3$, $[\text{Fe}(\text{CO})_4]\text{Na}_2$, $[\text{Fe}(\text{CO})_4]\text{Ca}$. These are formed both by direct *displacement* of hydrogen by the alkali or alkaline earth metals, dissolved in liquid ammonia, and by *neutralizing* the iron carbonyl hydride with solutions of the metal amides. The sparingly soluble alkaline earth salts can also be precipitated by double decomposition reactions—

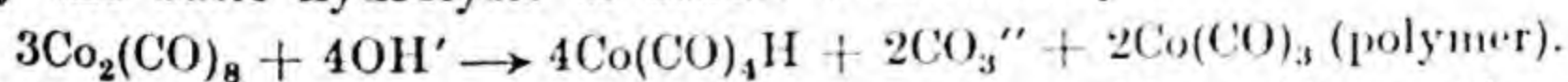


Iron carbonyl hydride thus behaves as a fairly strong acid in the ammonio-system of compounds.

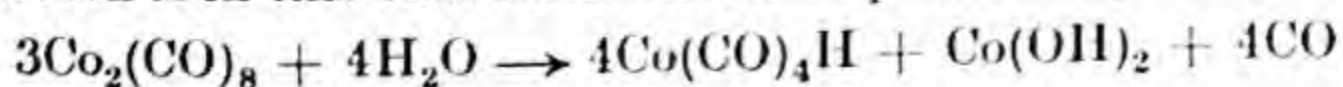
All the compounds mentioned above are true salts; they are characteristically decomposed by dilute acids, or even by water, forming the carbonyl hydride. By contrast, the metals of the zinc and copper groups form compounds with rather different properties, which should be regarded as polynuclear complex compounds, non-electrolytes. Hock and Stuhlmann's mercury iron tetracarbonyl belongs to this type, and can indeed be precipitated from iron carbonyl hydride by the addition of mercuric chloride. Similar reactions with ammoniacal zinc and cadmium solutions form the insoluble compounds $[\text{Fe}(\text{CO})_4][\text{Zn}(\text{NH}_3)_3]$, $[\text{Fe}(\text{CO})_4][\text{Cd}(\text{NH}_3)_2]$. There is a clear gradation of properties in this series of metal derivatives, as shown by their reactions with acids:



The valency rule governing the constitution of the metal carbonyls—*i.e.* that the effective atomic number of the metal atom is made up, by electron sharing, to the 'inert gas number'⁴²—suggests that intermediate between $\text{Fe}(\text{CO})_4\text{H}_2$ and $\text{Ni}(\text{CO})_4$ there should be a cobalt compound $\text{Co}(\text{CO})_4\text{H}$. Such a cobalt carbonyl hydride does, indeed, exist. It is formed, like iron carbonyl hydride, by the basic hydrolysis of cobalt tetracarbonyl:⁴³



The reaction is in this case somewhat complicated by a side reaction:



⁴² I. Langmuir, *Science*, 1921, 54, 65.

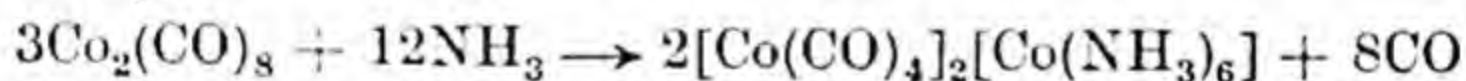
⁴³ W. Hieber, *Z. Elektrochem.*, 1934, 40, 158.

When ammonia is used for the hydrolysis in place of strong bases such as baryta or potash, the second mode of reaction alone comes into play.

The dilute solutions obtained by these hydrolytic reactions resemble in their chemical properties the solutions of iron carbonyl hydride. They reduce methylene blue, and yield cobalt tetracarbonyl by oxidation with atmospheric oxygen or with manganese dioxide.

By acidifying such a solution with phosphoric acid, Hieber and Schulten⁴⁴ prepared free $\text{Co}(\text{CO})_4\text{H}$. They condensed this out as a yellow crystalline solid, which melted at -26.2° and decomposed into cobalt tetracarbonyl and hydrogen at slightly higher temperatures. With an alcoholic solution of *o*-phenanthroline it formed the salt $[\text{Co}(\text{CO})_4]_2(\text{H}_2\text{.phth})$.

The precipitation reactions of cobalt carbonyl hydride are very similar to those of iron carbonyl hydride. Typical salts are formed with electropositive metals and with ammoniations—*e.g.* $[\text{Co}(\text{CO})_4]\text{Na}$, $[\text{Co}(\text{CO})_4]_2\text{Ca}$ from liquid ammonia; $[\text{Co}(\text{CO})_4]_2[\text{M}(\text{NH}_3)_6]$ from aqueous solutions. The rather soluble cobalt (ii) ammine salt $[\text{Co}(\text{CO})_4]_2[\text{Co}(\text{NH}_3)_6]$ is formed, in small amounts, during the hydrolysis of cobalt carbonyl by ammonia, due to the dissolution of some cobaltous hydroxide. It may be obtained also by the direct action of gaseous ammonia on cobalt tetracarbonyl:

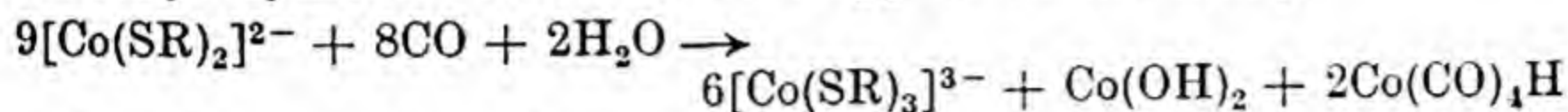


Compounds are also formed with the B sub-group metals—*e.g.* $[\text{Co}(\text{CO})_4]_2\text{Cd}$, $[\text{Co}(\text{CO})_4]_2\text{Hg}$. Like the analogous derivatives of iron carbonyl hydride, these are not salts. They are insoluble in water, but are soluble in organic solvents, in which they are monomeric.

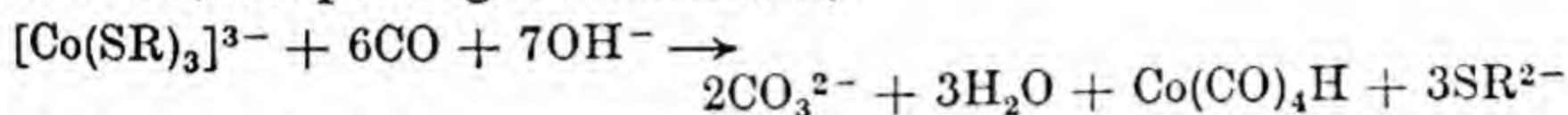
In addition to its preparation by the hydrolysis of cobalt carbonyl, cobalt carbonyl hydride is formed from cobalt (ii) salts in solution, by reactions very similar to those which produce nickel carbonyl. Thus cysteine, $\text{HS}\cdot\text{CH}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{COOH}$ (written as H_2SR), forms complex salts of the type $\text{K}_2[\text{M}(\text{SR})_2]$ with cobalt and ferrous iron; these are extremely sensitive towards oxygen, and their alkaline solutions absorb carbon monoxide. Whereas the ferrous cysteine complex forms the addition compound already mentioned, no addition compound can be isolated from the cobalt-cysteine system, although one molecule of CO is absorbed per atom of cobalt. The complex undergoes disproportionation instead, forming a cobalt (iii) compound, $\text{K}_3[\text{Co}(\text{SR})_3]\cdot 3\text{H}_2\text{O}$, as one product. If this salt be first

⁴⁴ *Z. anorg. Chem.*, 1937, 232, 17.

precipitated by means of acetone, the remaining solution yields the insoluble compounds $[\text{Co}(\text{CO})_4]_2\text{Hg}$, $[\text{Co}(\text{CO})_4]\text{Ag}$ when it is treated with mercuric chloride or silver nitrate.⁴⁵ It is therefore to be inferred that the second product of disproportionation is cobalt carbonyl hydride. The reactions appear to be, firstly,

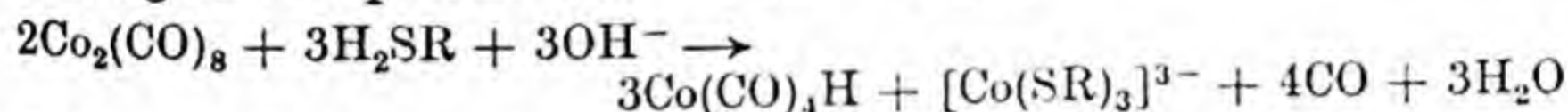


followed, on prolonged reaction, by



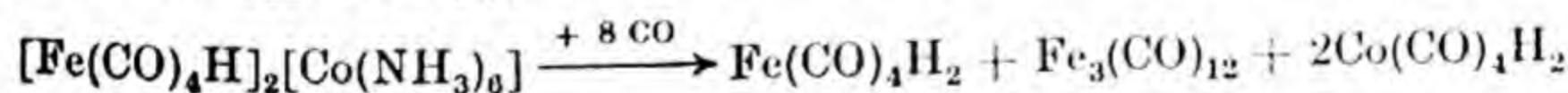
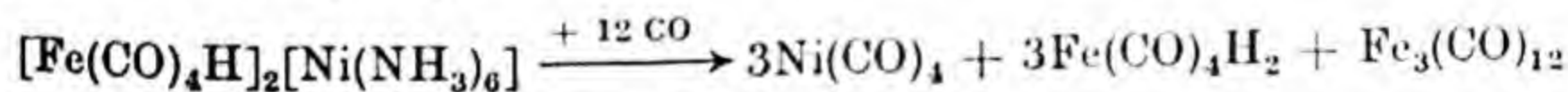
The nett effect of these reactions is to regenerate the cysteine, so that a small amount of cysteine suffices for the conversion of a considerably larger amount of cobalt (ii) salt to the carbonyl hydride.⁴⁶ In effect, the redox pairs $\text{Co}^{+2}/\text{Co}^{-1}$ and CO/CO_2 are catalytically coupled.

Valence disproportionations of this kind are not infrequently found. With cysteine in alkaline solution, cobalt carbonyl itself undergoes the process $4\text{Co}^0 \rightarrow \text{Co}^{+3} + 3\text{Co}^{-1}$:



Cobalt sulphide, xanthate and other thio-acid complexes behave similarly. If nitric oxide is admitted to these solutions after absorption of carbon monoxide, cobalt nitrosyl carbonyl, $\text{Co}(\text{CO})_3(\text{NO})$ (see below, p. 431), is produced.

Somewhat related to the processes just considered are the reactions of carbon monoxide with the metal ammine salts of iron carbonyl hydride.⁴⁷ These yield, as ultimate products, iron carbonyl hydride, iron tetracarbonyl and either nickel carbonyl or cobalt carbonyl hydride:



Some interest attaches to the reactions described, since they make it possible to obtain the carbonyls of nickel and cobalt by reactions occurring in solution. In view of the relative inaccessibility of cobalt carbonyl, these reactions might be useful in many laboratories. It is not yet known whether analogous methods could be applied to the convenient preparation of the carbonyls of the

⁴⁵ M. P. Schubert, *J. Amer. Chem. Soc.*, 1933, 55, 4563.

⁴⁶ G. W. Coleman and A. A. Blanchard, *J. Amer. Chem. Soc.*, 1936, 58, 2160.

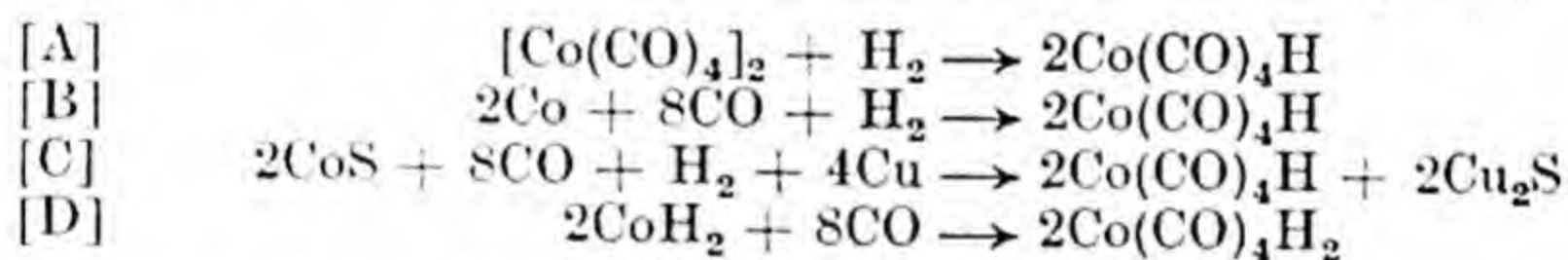
⁴⁷ W. Hieber, *Z. Elektrochem.*, 1937, 43, 390.

platinum metals—especially those of rhodium and iridium, which are closely analogous to cobalt carbonyl.

The Direct Synthesis of Cobalt Carbonyl Hydride.—The extreme ease with which cobalt carbonyl hydride is formed, in spite of its instability, is shown by its formation, in a variety of ways, in the high pressure carbonyl synthesis. Hieber, Schulten and Marin ²⁴ found that in the synthesis of cobalt carbonyl, the gases blown off from the autoclave occasionally contained a volatile cobalt compound, and they showed this to be the carbonyl hydride by precipitating $[\text{Co}(\text{CO})_4]\text{HgCl}$ from mercuric chloride solution. It was formed only when the reactants contained traces of water, and by deliberately moistening the cobalt sulphide or iodide used for the synthesis, the yield could be increased :



It was found, moreover, that the carbonyl hydride could be synthesized directly from its components in a variety of ways—*e.g.* by heating cobalt carbonyl in hydrogen and carbon monoxide under pressure [A], by the simultaneous action of hydrogen and carbon monoxide on metallic cobalt [B], by carrying out the indirect carbonyl synthesis in the presence of hydrogen—[C], or by the action of carbon monoxide on Weichselfelder's cobalt hydride ⁴⁸ [D].



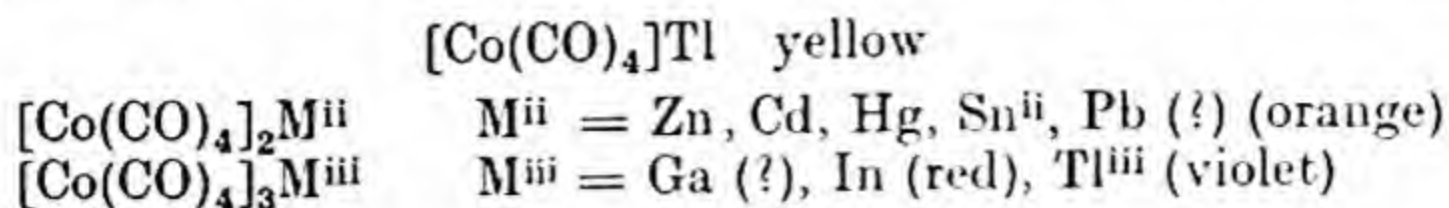
Reaction [A] is the converse of the spontaneous decomposition of cobalt carbonyl hydride, occurring at the ordinary pressure ; this is therefore a truly reversible process.

High pressure syntheses of this kind are not limited to cobalt carbonyl hydride. $\text{Rh}(\text{CO})_4\text{H}$, $\text{Ir}(\text{CO})_4\text{H}$, $\text{Os}(\text{CO})_4\text{H}_2$ and probably $\text{Re}(\text{CO})_5\text{H}$ have also been formed by similar processes. By contrast, iron carbonyl hydride is obtained only by hydrolysis reactions in aqueous solution ; in high pressure syntheses, iron pentacarbonyl is the only product.

The ease with which cobalt carbonyl hydride is formed extends also to its heavy metal derivatives. When the metals of the B-subgroups are used as halogen acceptors in the high pressure synthesis, or when their halides are heated with cobalt metal and carbon monoxide, the product of the reaction is not $[\text{Co}(\text{CO})_4]_2$, but the corresponding metal derivative, identical with that obtain-

⁴⁸ *Annalen*, 1926, 447, 64.

able from solutions of cobalt carbonyl hydride. The compounds



have been prepared in this manner.⁴⁹

Substitution Reactions of the Metal Carbonyls.—It is a characteristic property of the metal carbonyls and their derivatives (other than the carbonyl hydrides) that the carbon monoxide may be replaced by other neutral molecules, such as amines or thioethers. A large variety of compounds is so formed which, like the unsubstituted carbonyls, appear to be bound entirely by co-ordinative valence forces.

It is convenient to consider first the behaviour of the iron carbonyls. In accordance with the relative inertness of the mono-metallic carbonyls generally, iron pentacarbonyl reacts only sluggishly with substituents. Neither ammonia nor ethylene diamine effects substitution under ordinary conditions; they form addition compounds $\text{Fe}(\text{CO})_5\text{NH}_3$, $\text{Fe}(\text{CO})_5\text{en}$. The formation of such addition compounds is a preliminary step of frequent occurrence (*cf.* the formation of $\text{Fe}(\text{CO})_5\text{I}_2$, $\text{Fe}(\text{CO})_5\text{Hg}(\text{OAc})_2$), but the amine compounds are peculiar in that they break down, on treatment with acids, into iron tetracarbonyl (or possibly iron carbonyl hydride) and a ferrous salt.

Pyridine reacts slowly with iron pentacarbonyl at 80° , giving a compound, $\text{Fe}_2(\text{CO})_4\text{pyr}_3$.⁵⁰ This, like many of the substituted carbonyls, absorbs oxygen so avidly as to be pyrophoric; it is completely decomposed by bromine, but iodine at -21° , or cyanogen at 60° , form the same compounds, $\text{Fe}(\text{CO})_2\text{pyr}_2\text{I}_2$ and $\text{Fe}(\text{CO})_2\text{pyr}(\text{CN})_2$, as are obtained by the action of pyridine on the iron carbonyl halides. In the presence of pyridine, other amines also displace carbon monoxide, ammonia then forming $\text{Fe}(\text{CO})_3(\text{NH}_3)_2$, and ethylene diamine giving $\text{Fe}_2(\text{CO})_5\text{en}_2$. The latter behaves as if it had the constitution $\text{Fe}(\text{CO})_5\text{Fe en}_2$, since it gives equivalent amounts of iron pentacarbonyl, ferrous salt and hydrogen when it is decomposed by acids.

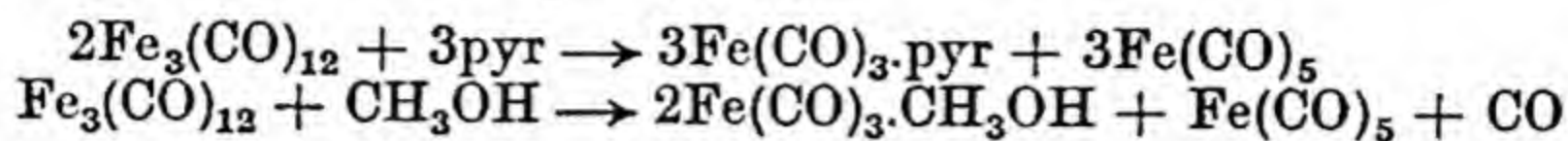
The greater reactivity of iron tetracarbonyl, $\text{Fe}_3(\text{CO})_{12}$, leads to reaction under milder conditions than with the pentacarbonyl,⁵¹ so that the initial product is usually a tricarbonyl derivative $\text{Fe}(\text{CO})_3\text{X}$ (where $\text{X} = \text{pyridine, } o\text{-phenanthroline, CH}_3\text{OH, CH}_3\text{CN, etc.}$), rather than a dicarbonyl derivative, as is frequently the case in the

⁴⁹ W. Hieber and U. Teller, *Z. anorg. Chem.*, 1942, 249, 43.

⁵⁰ W. Hieber *et al.*, *Ber.*, 1928, 61, 2421; 1930, 63, 973.

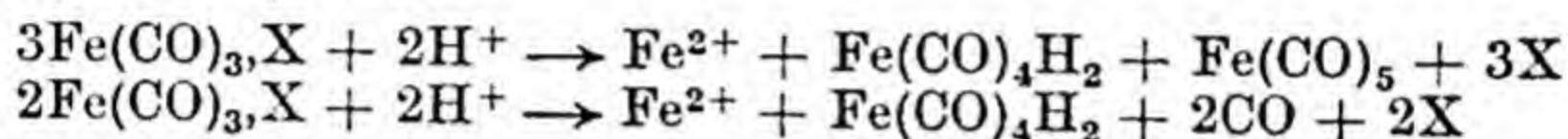
⁵¹ *Idem, ibid.*, 1930, 63, 1405; 1931, 64, 2340.

reactions of iron pentacarbonyl. The further reactions of substituents may then lead to compounds with lower ratios of Fe : CO. In the substitution reactions, iron pentacarbonyl is always formed to the extent of 33–50 per cent :



The formation of iron pentacarbonyl may signify that a $\text{Fe}(\text{CO})_4$ radical (the existence of which has been assumed on photochemical grounds) is formed transiently in the reactions, and is reduced by nascent carbon monoxide.

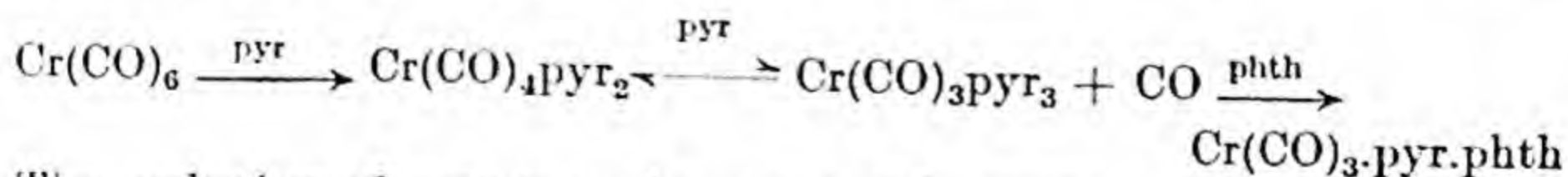
The redistribution of carbonyl groups illustrated above is typical of the reactions of these compounds, as also is a disproportionation into Fe^{2+} and iron carbonyl hydride when the compounds are decomposed by acid :



The ethylene diamine derivative $\text{Fe}_2(\text{CO})_4\text{en}_3$ reacts with acids to give equivalent amounts of ferrous salt and iron carbonyl hydride, and thus behaves as if it were the salt of iron carbonyl hydride with a complex cation, $[\text{Fe}(\text{CO})_4][\text{Fe en}_3]$. However, Hieber and Fack found that they could not prepare salts of the analogous complex cations $[\text{Co en}_3]^{2+}$, $[\text{Ni en}_3]^{2+}$, and concluded that $\text{Fe}_2(\text{CO})_4\text{en}_3$ is to be regarded as a pure co-ordination compound. It is not possible to formulate most of the substituted carbonyls as salt-like derivatives of iron carbonyl hydride.

Carbonyls of other metals give rise to similar series of derivatives. Thus, the action of pyridine on nickel carbonyl⁵² ultimately yields $\text{Ni}_2(\text{CO})_3\text{pyr}_2$; the displacement of carbon monoxide by pyridine is a reversible reaction, illustrating the mobility of the metal-CO system. With *o*-phenanthroline, nickel carbonyl forms the very stable $\text{Ni}(\text{CO})_2\text{phth}$.

The hexacarbonyls of chromium, molybdenum and tungsten show a greater regularity in their substitution products,⁵³ in that their composition is, for the most part, such as to maintain the co-ordination number 6.

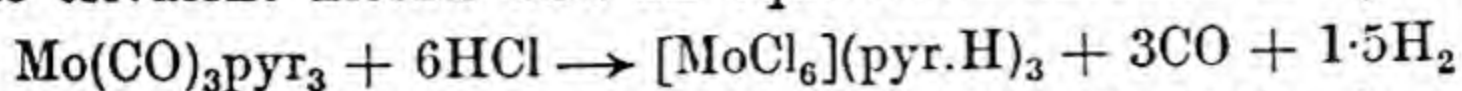


The substituted compounds are much more reactive than the

⁵² *Idem, ibid.*, 1932, 65, 1090.

⁵³ W. Hieber and F. Muhlbauer, *Z. anorg. Chem.*, 1935, 221, 337; Hieber and Romberg, *ibid.*, 1935, 221, 349.

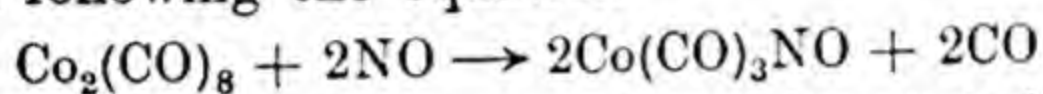
hexacarbonyls; they are decomposed by acids, forming compounds of the trivalent metals and an equivalent amount of hydrogen:



Similar compounds (*e.g.* $\text{Re(CO)}_3\text{pyr}_2$, $\text{Re(CO)}_3\text{phth}$) have also been obtained from rhenium carbonyl, but the detailed chemical behaviour of the recently discovered carbonyls remains to be investigated.

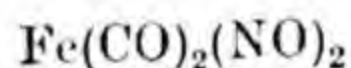
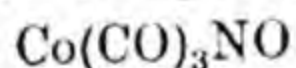
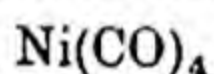
NITROSYL CARBONYLS AND METAL NITROSYL DERIVATIVES

Nitrosyl Carbonyls.—Nitric oxide reacts with the polynuclear carbonyls of cobalt and iron, forming volatile red liquids which are the nitrosyl carbonyl compounds $\text{Co(CO)}_3\text{NO}$ ⁵⁴ and $\text{Fe(CO)}_2(\text{NO})_2$ ⁵⁵ respectively. The reaction with cobalt carbonyl is practically quantitative, following the equation



The formation of cobalt nitrosyl carbonyl by an indirect reaction, presumably involving the disproportionation of $\text{K}_3[\text{Co(CN)}_5\text{CO}]$, has been referred to on an earlier page. Both iron nonacarbonyl and iron tetracarbonyl undergo a rather complex reaction with nitric oxide, whereby iron pentacarbonyl and the nitrosyl carbonyl are formed simultaneously.

It may be seen that the metals nickel, cobalt and iron thus form a graded series of volatile compounds,



in which, as the atomic number of the central atom is decreased, carbon monoxide is replaced step by step by nitric oxide. The physical properties of these substances show a corresponding steady gradation, which reflects the increasing dipole moment introduced by the substitution of NO for CO (Table 5).

Table 5

	Ni(CO)_4	$\text{Co(CO)}_3\text{NO}$	$\text{Fe(CO)}_2(\text{NO})_2$
Boiling-point	43°	78.6°	[110°]
Freezing-point	− 23°	− 1.1°	+ 18.4°
Trouton's const.	21.9	22.6	24.0
Density at 20°	1.31	1.47	1.56
Parachor	255.3	249.8	252.5
Zero-point volume	94.4	91.1	87.6

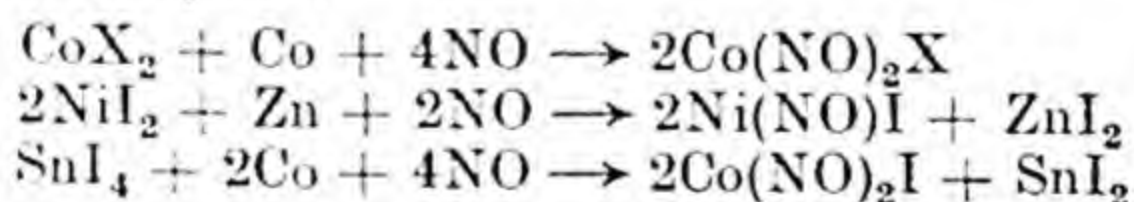
⁵⁴ R. Mond and A. Wallis, *J.C.S.*, 1922, 121, 34.

⁵⁵ J. S. Anderson, *Z. anorg. Chem.*, 1932, 208, 238.

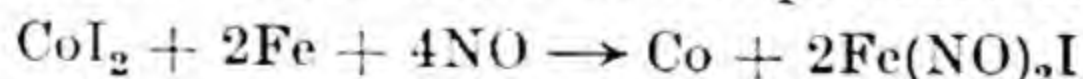
The carbon monoxide in the nitrosyl carbonyls is replaceable by other neutral molecules, just as in the carbonyls, but in these substitution reactions the nitrosyl group is not displaced.⁵⁶ The resemblance of the compounds to nickel carbonyl is exemplified further in that reaction with pyridine, leading to the compounds $\text{Co}_2(\text{NO})_2(\text{CO})\text{pyr}_2$ and $\text{Fe}_2(\text{NO})_4\text{pyr}_3$, is reversible and incomplete, while reaction with *o*-phenanthroline forms the stable compounds $\text{Fe}(\text{NO})_2\text{phth}$ and $\text{Co}(\text{NO})(\text{CO})\text{phth}$. Here again, comparison with the nickel compound $\text{Ni}(\text{CO})_2\text{phth}$ shows a step-by-step replacement of carbon monoxide by nitric oxide, while preserving the same structural type.

Iodine also displaces carbon monoxide from iron nitrosyl carbonyl, forming iron dinitrosyl iodide, $\text{Fe}(\text{NO})_2\text{I}$. The nitrosyl carbonyls are thereby linked with other iron nitrosyl compounds, and especially with the 'red salts of Roussin', $\text{Fe}(\text{NO})_2\text{SR}$, which are likewise derived from the univalent radical $\text{Fe}(\text{NO})_2-$.

More recent work⁵⁷ has shown some rather close analogies between the chemistry of the nitrosyl compounds and that of the carbonyls. $\text{Fe}(\text{NO})_2\text{I}$ can be prepared by the direct reaction of nitric oxide with ferrous iodide or iron carbonyl iodide, as well as in the manner cited above. If finely divided carbonyl iron is present as a halogen acceptor, the analogous bromide $\text{Fe}(\text{NO})_2\text{Br}$ and the volatile trinitrosyl iron chloride $\text{Fe}(\text{NO})_3\text{Cl}$ can be prepared by similar methods. Volatile, covalent nitrosyl monohalides, $\text{Co}(\text{NO})_2\text{X}$ and $\text{Ni}(\text{NO})\text{X}$, are formed by cobalt and nickel also. These may all be prepared by reactions typically similar to those of the high pressure carbonyl synthesis, involving the metal halide and a halogen acceptor:



The ease of formation of these compounds increases in the sequence $\text{Ni} < \text{Co} < \text{Fe}$ and $\text{X} = \text{Cl} < \text{Br} < \text{I}$, so that $\text{Fe}(\text{NO})_2\text{I}$ is the most stable and most readily formed. This is the sole product of reaction of nitric oxide with cobalt iodide in the presence of metallic iron:



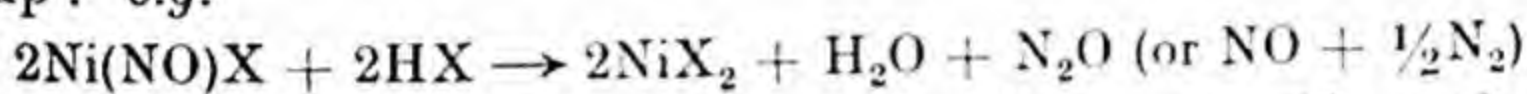
The monometallic carbonyls react with nitric oxide in quite a different manner from the polynuclear iron and cobalt carbonyls, for reaction occurs only when it can be accompanied by simultaneous oxidation. The very stable hexacarbonyls of chromium, molyb-

⁵⁶ W. Hieber and J. S. Anderson, *ibid.*, 1933, 211, 132.

⁵⁷ Hieber and Nast, *Z. anorg. Chem.*, 1940, 244, 23; Hieber and Marin, *ibid.*, 1939, 240, 241.

denum and tungsten are quite inert, and the reaction of iron carbonyl has not been properly elucidated. Solutions of nickel carbonyl in inert solvents, however, react with nitric oxide to form a blue amorphous substance, in very small amount; this is soluble in, and decomposed by, water, and has been shown to have the composition Ni(NO)OH .⁵⁸ It appears to owe its formation to traces of moisture adventitiously present. When dissolved in methyl or ethyl alcohol, nickel carbonyl reacts almost quantitatively with nitric oxide, forming similar blue compounds $\text{Ni(NO)OCH}_3 \cdot \text{CH}_3\text{OH} \cdot \text{H}_2\text{O}$, $\text{Ni(NO)OC}_2\text{H}_5 \cdot \text{H}_2\text{O}$. These need further investigation, but it would appear that all are derived from the same univalent Ni(NO)^- radicle that is present in the nickel nitrosyl halides. The principal chemical properties of all the compounds are similar.

They are decomposed by acids, the formally univalent metal being oxidized to the bivalent state at the expense of the nitrosyl group: *e.g.*



The nickel nitrosyl compounds react with the cyanide and thio-sulphate ions to form the salts of complex nitrosyl anions—*e.g.* $\text{K}_3[\text{Ni(NO)(S}_2\text{O}_3)_2] \cdot 2\text{H}_2\text{O}$ and $\text{K}_2[\text{Ni(NO)(CN)}_3]$. The latter is identical with the salt formed by the action of nitric oxide on Belucci's $\text{K}_2[\text{Ni(CN)}_3]$.

With amines, the metal nitrosyl derivatives may react either additively, as in the formation of $\text{Ni(NO)I} \cdot 2\text{phth}$ from Ni(NO)I , or by substitution of nitrosyl groups by amine molecules. Thus iron dinitrosyl iodide reacts with pyridine to form $\text{Fe(NO)(pyr)}_6\text{I}$. In this respect they differ from the nitrosyl carbonyls; in these compounds the replacement of carbonyl groups by neutral molecules takes place readily, but the displacement of nitrosyl groups has not been observed. With an excess of amines capable of forming very stable complex cations, complete decomposition and intramolecular oxidation can occur. Thus an excess of ortho-phenanthroline converts the iron nitrosyl derivatives to salts of the $[\text{Fe phth}_3]^{2+}$ cation, nitrosyl groups being lost as N_2O in the process.

The Constitution of the Metal Carbonyls.—Since the discovery of the metal carbonyls, their constitution has presented a problem in every development of the theory of valency. Their non-polar character (to which they owe their volatility), and the diamagnetism of the simple carbonyls and all their substitution products, stand in contrast with the properties of other classes of compound formed by the transition elements. The formal valency

⁵⁸ J. S. Anderson, *Z. anorg. Chem.*, 1936, 229, 357.

of the metals in the carbonyls is not immediately apparent, but there is evidently some simple systematic relation between the atomic numbers of the metals and the composition of their simplest carbonyls.

These considerations rule out older speculative views, which sought to retain the normal valencies of the carbonyl-forming metals. The accepted view, that carbon monoxide is in some way linked or co-ordinated with the metal atom (as are the ammonia molecules in a complex ammine), was foreseen in a sense by Ludwig Mond, in his first account of the compounds in 1892.

This conception carries with it the implication that the CO groups exist as such within the molecules, and that they retain much the same bond character as in the free carbon monoxide molecule. The first point is attested by the ease with which carbon monoxide is liberated as such, and by the step-by-step replacement of carbonyl groups by neutral molecules—every successive stage of replacement being capable of realization in certain instances, such as in the iron carbonyl halides.

Several lines of evidence lend support to the second conclusion. Sutton and Bentley⁵⁹ found nickel carbonyl to have a zero dipole moment. This implies that the M—C—O group must be collinear, since the free rotation of bent groups would confer on the molecule a resultant dipole moment, such as is found for C(OEt)₄.

Unless the metal-CO link is ketenic in nature, M=C=O, which would involve very high covalencies in Fe(CO)₅ or Cr(CO)₆, this is compatible only with a triple C≡O link, such as exists in carbon monoxide itself. The Raman spectrum of nickel carbonyl lends support to this view, for the strongest Raman line corresponds to a displacement of 2,039 cm.⁻¹, compared with a shift of 2,155 cm.⁻¹ in the Raman spectrum of carbon monoxide. Comparison of these figures with the Raman shifts characteristic of double and triple bonds, respectively, shows that a triple bond is present both in carbon monoxide and in the carbonyls.⁶⁰ Recent measurements of bond lengths, by the electron diffraction method, are also in accord with this conclusion, though they indicate also that the M—C and C—O bonds are probably not pure single and triple bonds respectively; they may perhaps be resonance hybrids, in which (especially in nickel carbonyl) the ketenic form is not unimportant.

It is permissible, therefore, to regard the CO group in the carbonyls as a little-modified carbon monoxide molecule, co-ordinated to a central metal *atom*, as other neutral molecules or ions are linked, in complex salts, to central *cations*. The existence of the

⁵⁹ *J.C.S.*, 1933, 652.

⁶⁰ J. S. Anderson, *Nature*, 1932, 130, 1002

simplest carbonyl compound, borine carbonyl, BH_3CO , which is exactly analogous to $\text{BH}_3\text{N}(\text{CH}_3)_3$, shows that the carbon monoxide molecule can act as a co-ordinating group in this way.

On the view that carbon monoxide is co-ordinatively bound to the central atoms, an important rule, first pointed out by Langmuir, emerges governing the composition of the monometallic carbonyls. In each case the number of carbon monoxide molecules is such as to make the effective atomic number of the metal, on Sidgwick's conception of the co-ordinate link, up to that of the next inert gas (Table 6).

Table 6

$\text{Ni}(\text{CO})_4$	E.A.N. = $28 + 4 \times 2 = 36$
$\text{Fe}(\text{CO})_5$	$26 + 5 \times 2 = 36$
$\text{Cr}(\text{CO})_6$	$24 + 6 \times 2 = 36$
$\text{Mo}(\text{CO})_6$	$42 + 6 \times 2 = 54$
$\text{Ru}(\text{CO})_6$	$44 + 5 \times 2 = 54$

It is significant that the elements of odd atomic number, Co, Rh, Re, Ir, form no monometallic carbonyls. The requisite condition of molecular stability has to be achieved by some further formation of co-ordinate links within binuclear molecules.

The molecular configuration of the monometallic carbonyls is also of interest, since on Pauling's view the steric arrangement about the central atom provides evidence of the type of hybrid bond orbitals involved. For the hexacarbonyls of chromium, molybdenum and tungsten it has been shown by X-ray crystal structure methods that, as would be expected, the carbon monoxide is closely co-ordinated in an octohedral configuration about the metal atom. The metal-CO distance, which affords a measure of the tightness of binding of the CO, increases from chromium to tungsten to a greater extent than corresponds with the increase in atomic radius, in keeping with the perceptible decrease in stability of the carbonyls.⁶¹

Nickel carbonyl provides an interesting stereochemical comparison with other nickel complexes in that it is derived, not from a Ni^{2+} ion, but from a neutral nickel atom with a completed $3d$ quantum shell. It is thus isoelectronic with the $[\text{Zn}(\text{CN})_4]^{2-}$ ion. On Pauling's theory, the co-ordinate links must therefore be formed from the hybridized $4s4p^3$ orbits, and should lead to the tetrahedral configuration which is, indeed, found for the $[\text{Zn}(\text{CN})_4]^{2-}$ ion. The tetrahedral configuration of nickel carbonyl so predicted has been inferred independently from the nature of its Raman spectrum, and has been confirmed by Brockway and Cross⁶² from the electron diffraction study of nickel carbonyl vapour.

⁶¹ E. Rüdorff and U. Hoffmann, *Z. physikal. Chem.*, B, 1935, 28, 351.

⁶² *J. Chem. Physics*, 1935, 3, 828.

These views may be extended to the closely allied nitrosyl carbonyls. A $(\text{NO})^+$ group would have the same number of electrons as neutral CO, or as the $(\text{CN})^-$ ion, and so could be written with the same triple-bonded structure. Since neutral nitric oxide has one electron more than has carbon monoxide, the formation of a metal nitrosyl compound can be regarded as involving first the transfer of an electron from the NO group to the metal, followed by co-ordination of the $(\text{N}\equiv\text{O})^+$ group thereby resulting. The effective atomic number of the metal atom is thereby increased, and its electrovalency, if an ion, is decreased, each by one unit. In an exactly similar way, the co-ordination of a $(\text{CN})^-$ group raises the electrovalency by one unit. It is thus clear why the nitrosyl carbonyls of cobalt and iron conform to the same structural type as nickel carbonyl; in each case, the central atom becomes a 'pseudo-nickel' atom.

$\text{Ni}(\text{CO})_4$	Total E.A.N. of metal atom = $28 + 4 \times 2$	= 36
$\text{Co}(\text{CO})_3\text{NO}$		= $27 + 3 + 3 \times 2$ = 36
$\text{Fe}(\text{CO})_2(\text{NO})_2$		= $26 + 6 + 2 \times 2$ = 36

The same conformity to the structural type of the nickel carbonyl compound is seen in the *o*-phenanthroline compounds $\text{Ni}(\text{CO})_2\text{phth}$, $\text{Co}(\text{CO})(\text{NO})\text{phth}$, $\text{Fe}(\text{NO})_2\text{phth}$.

This rule relating to the co-ordination of NO, CO and CN groups applies quite generally, and is not restricted to the carbonyl compounds. This may be seen from a consideration of the 6-co-ordinated pentacyano compounds of a number of metals (Table 7).

Table 7

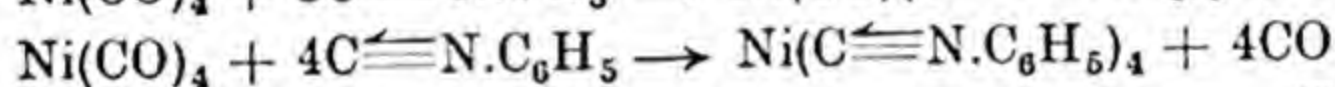
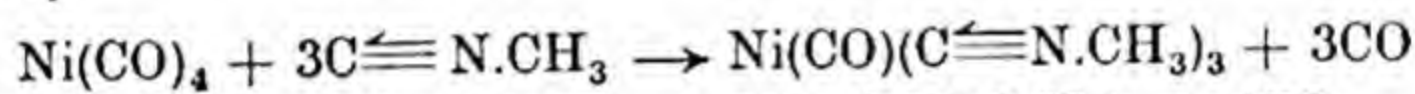
$M-(\text{NO})^+$	$M-(\text{CO})$	$M-(\text{CN})^-$
$\text{K}_3[\text{Mn}(\text{CN})_5\text{NO}]$		$\text{K}_5[\text{Mn}(\text{CN})_6]$
$\text{K}_2[\text{Fe}(\text{CN})_5\text{NO}]$	$\text{K}_3[\text{Fe}(\text{CN})_5\text{CO}]$	$\text{K}_4[\text{Fe}(\text{CN})_6]$
	$\text{K}_3[\text{Fe}(\text{CN})_5\text{NH}_3]$	
$\text{K}_2[\text{Ru}(\text{CN})_5\text{NO}]$		$\text{K}_4[\text{Ru}(\text{CN})_6]$
$\text{K}_2[\text{RuCl}_5\text{NO}]$		
$\text{K}_2[\text{OsCl}_5\text{NO}]$		$\text{K}_4[\text{OsCl}_6]$

Metal Cyanyls and Isonitriles.—The equivalence of the $:\text{C}::\text{N}:^-$ and $:\text{C}::\text{O}:^+$ groups in the complex cyanides (Table 6) prompts the question whether these groups are also interchangeable in the carbonyls proper. This is, in fact, the case. Eastes and Burgess⁶³ found that the reduction of $\text{K}_2[\text{Ni}(\text{CN})_4]$ by metallic potassium in liquid ammonia produced a complex salt of zero-valent

⁶³ *J. Amer. Chem. Soc.*, 1942 **64**, 1187.

nickel, $K_4[Ni(CN)_4]$. This is equivalent in electronic structure to nickel carbonyl, although the $C-N^-$ groups confer on the complex an anionic charge. It might appropriately be termed a nickel cyanyl.

Electrostatically neutral analogues of this type of compound might be formally derived from the isonitriles, $R-N\equiv C$; the nitriles do not come into question, since co-ordination is effected through the carbon atom in the carbonyls and the cyano-complexes. The compound $[Fe(CN)_2(CN.CH_3)_4]$, which has been known for a long time,⁶⁴ is of this type. Hieber and Böckly⁶⁵ have recently shown that isonitrile groups can displace CO groups from the metal carbonyls, forming derivatives of considerable stability. In the case of nickel carbonyl, the process can indeed be carried to the limit, all the CO groups being displaced to form nickel tetraphenyl isonitrile, $[Ni(C\equiv N.C_6H_5)_4]$, a yellow, extremely stable compound which may well be the precursor of a new field of transition metal chemistry.



Nickel Compounds of Phosphorus Trihalides.—The possibility of preparing 'pure co-ordination' compounds analogous to the carbonyls is not restricted to the replacement of CO by isoelectronic groups. Chatt⁶⁶ has advanced reasons for supposing that PCl_3 and PF_3 bear some resemblance to CO as co-ordinating groups, and that both differ in certain respects from ammonia, the co-ordination of which is satisfactorily interpreted in terms of the 'lone pair' hypothesis. Thus CO and PCl_3 both form very unstable compounds with BF_3 , but extremely stable compounds with $PtCl_2$, whereas ammonia forms stable, non-volatile compounds with both BF_3 and $PtCl_2$. PF_3 , in particular, forms the volatile compounds $[PtCl_2(PF_3)_2]$, $[PtCl_2(PF_3)]_2$, which show a marked resemblance to Schützenberger's carbonyl platinous chlorides.

This similarity between the PX_3 and the CO groups has now been shown to extend to the metal carbonyls also. PCl_3 reacts readily with nickel carbonyl, displacing all the CO groups and forming a yellow, non-volatile compound $Ni(PCl_3)_4$.⁶⁷ PF_3 effects only a partial and reversible displacement of CO from nickel carbonyl, but will combine directly with metallic nickel to form

⁶⁴ Hartley, *J.C.S.*, 1913, 103, 1196; 1916, 105, 331; Powell and Bartindale, *ibid.*, 1945, 799.

⁶⁵ *Z. anorg. Chem.*, 1950, 262, 344.

⁶⁶ J. Chatt, *Nature*, 1950, 165, 637.

⁶⁷ J. W. Irvine, Jr., and G. Wilkinson, *Science*, 1951, 113, 742.

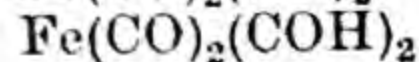
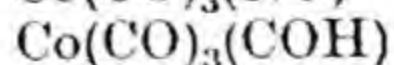
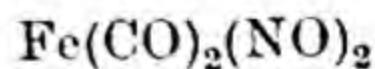
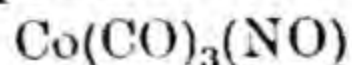
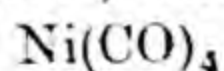
$\text{Ni}(\text{PF}_3)_4$, although this compound is most readily obtained by displacing PCl_3 from $\text{Ni}(\text{PCl}_3)_4$ by means of phosphorus trifluoride under pressure.

Tetra(phosphorus trifluoride) nickel is a colourless, mobile, diamagnetic liquid, m.p. -55° , boiling at 70.7° , with a density of 1.800 at 25° . It thus resembles nickel carbonyl in physical properties, but is more stable and rather less reactive. The properties of the co-ordinated PF_3 and PCl_3 groups in these compounds are so far modified that hydrolysis occurs only slowly, so that $\text{Ni}(\text{PF}_3)_4$ may be vaporized in the presence of steam.⁶⁸ There is some evidence that the PF_3 compound, like nickel carbonyl, reacts with pyridine by partial displacement of the PF_3 groups.

Other Group VB halides appear to have potentially the same co-ordinating properties, and Wilkinson⁶⁸ has found that antimony trichloride may also displace CO from metal carbonyls. The compounds $\text{Ni}(\text{CO})_3\text{SbCl}_3$ and $\text{Fe}(\text{CO})_3(\text{SbCl}_3)_2$ have been isolated by this means.

It was suggested by Chatt (*loc. cit*) that it is characteristic of the stable co-ordinations of CO, of PF_3 , etc., and probably of olefins, that they are formed only by transition metals with filled d orbitals. This could make possible a sort of back-co-ordination, between filled d -orbitals of the metal atom and vacant orbitals or π -orbitals of the co-ordinated group. This would produce a π -type dative bond, operating in addition to the (σ -type) lone pair co-ordinate link—an idea already adumbrated by Hieber.⁶⁹ It may be significant that the dimensional evidence points to a considerable measure of double bond character in the nickel-CO linkage of nickel carbonyl.

Carbonyl Hydrides and Polynuclear Carbonyls.—Iron and cobalt carbonyl hydrides have been shown⁷⁰ to have the same tetrahedral molecular configuration as is possessed by $\text{Ni}(\text{CO})_4$. It is not certain, however, how the hydrogen is bound in these molecules. Ewens and Lister suggested that it is linked to oxygen, to make a grouping $(:\text{C}::\text{O}:\text{H})^+$ which is isoelectronic with the $(:\text{N}::\text{O}:)^+$ grouping, and therefore with $(:\text{C}::\text{O}:)$. The parallelism between the formation and the constitution of carbonyl hydrides and of nitrosyl carbonyls follows naturally from this plausible hypothesis, but rigorous proof is lacking:—



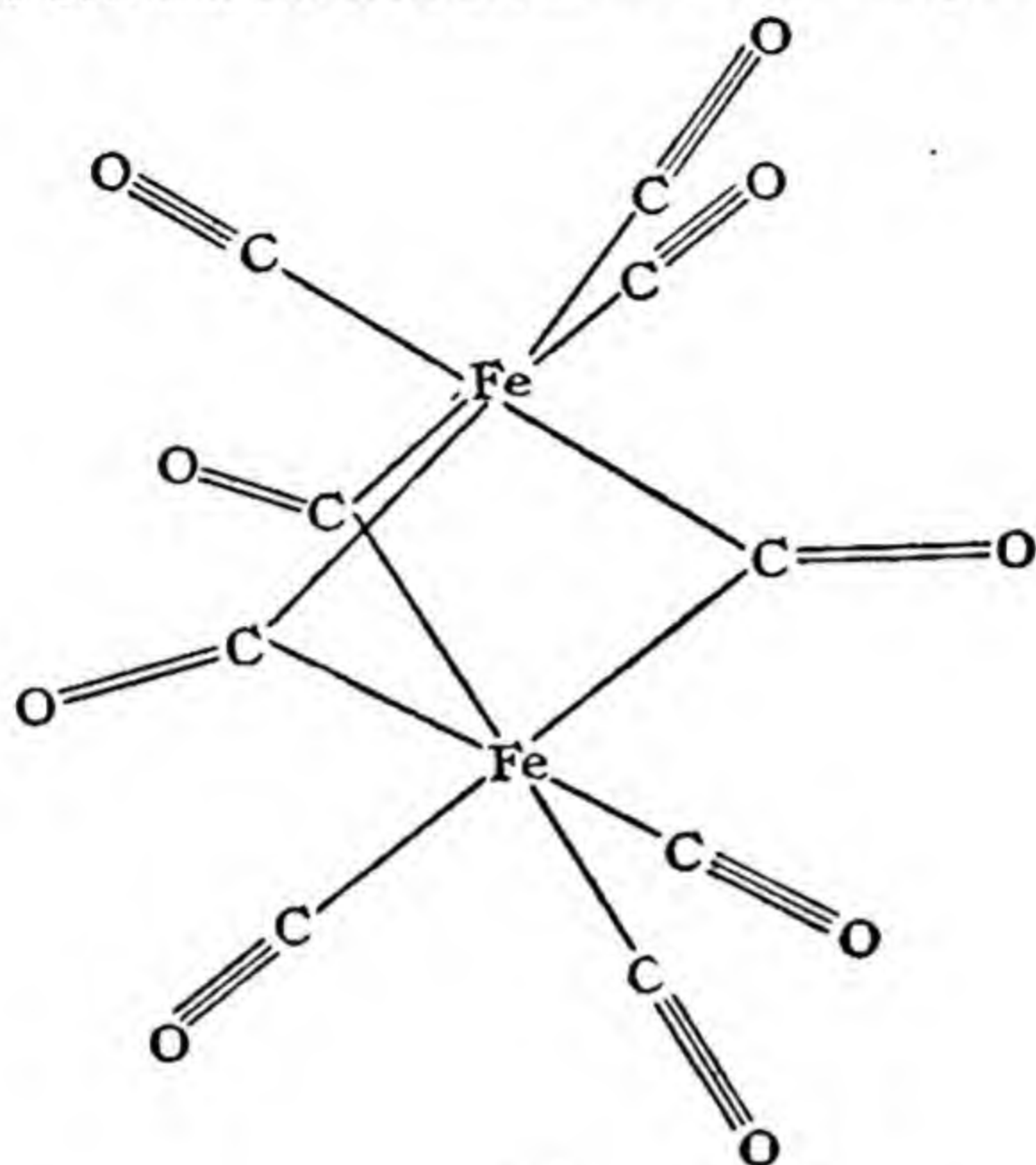
There is no doubt that some CO groups act as bridges between

⁶⁸ G. Wilkinson, 1951, private communication.

⁶⁹ W. Hieber, *Angew. Chem.*, 1942, 55, 25.

⁷⁰ R. V. G. Ewens and M. W. Lister, *Trans. Faraday Soc.*, 1939, 35, 681.

the metal atoms of the polynuclear carbonyls, but only in the case of $\text{Fe}_2(\text{CO})_9$ has the structure been determined experimentally⁷¹ with any completeness. In this compound, three CO groups are linked, as bridge groups, to both atoms of iron, as in structure (I). The distance between the iron atoms would be compatible with an



(I)

additional covalent bond between the iron atoms. The apparent implication of this structure is that the polynuclear carbonyls contain two fundamentally distinct kinds of CO-groups: true metal carbonyl groups, $\text{M} \leftarrow \text{C} \equiv \text{O}$, and groups essentially similar in nature

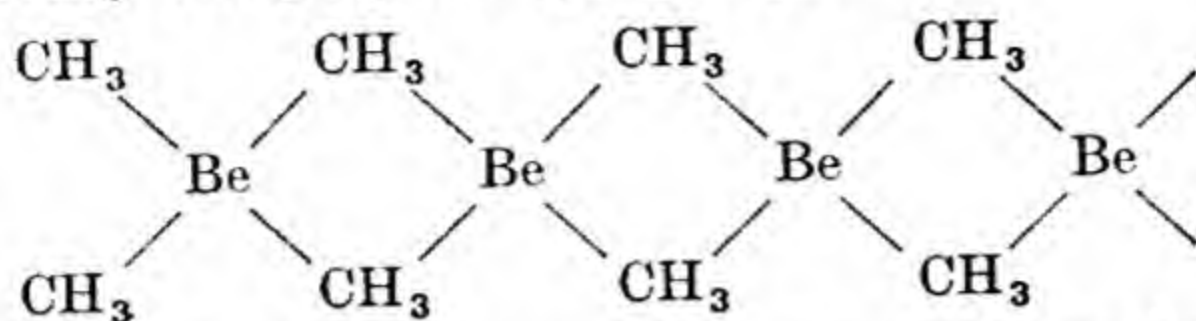
to the carbonyl groups of ketones, $\begin{array}{c} \text{M} \\ \diagdown \\ \text{C} = \text{O} \\ \diagup \\ \text{M} \end{array}$. It would also appear

that the iron atoms in $\text{Fe}_2(\text{CO})_9$ (and presumably in $\text{Fe}_3(\text{CO})_{12}$ also, which is believed to have a sterically analogous bridged structure) are not zero-valent, but trivalent. It will be apparent from the earlier portions of this chapter that there is no chemical evidence to indicate any vital constitutional difference between the mono-metallic and the polynuclear carbonyls.

It is possible that the facts could be harmonized by the concept of electron-deficient bonds, in the form already invoked to explain

⁷¹ H. M. Powell and R. V. G. Ewens, *J.C.S.*, 1939, 286.

the constitution of the polymeric metal alkyls. Thus Snow and Rundle ⁷² have found that dimethyl beryllium is made up of linear chains involving bridging methyl groups:



They regard the bridge groups as tetrahedral methyl groups in which one of the tetrahedral bond orbitals is directed symmetrically between the two neighbouring beryllium atoms, and suppose that this orbital overlaps orbitals of both beryllium atoms. The three orbitals involved combine to form a single molecular orbital which is, however, tenanted by only one electron pair. The bonds are thus of fractional order; there may, in addition, be some measure of metal-metal bonding. The validity of this model has not been established, but if it may be extended to the polynuclear carbonyls we could consider one orbital of the CO group (that containing the lone pair of electrons) as overlapping symmetrically a vacant orbital of each metal atom.

It is probably safe to conclude that although the spatial arrangement of the atoms has been found, the bond pattern in the typical polynuclear carbonyls is uncertain. The constitution of these compounds must still be accounted amongst the unsolved problems of molecular structure.

⁷² *Acta Cryst.*, 1951, 4, 348.

CHAPTER XV

METALS AND INTERMETALLIC COMPOUNDS

Most chemical compounds conform to the simple rules which are explicable in terms of the electronic theory of valency outlined in an earlier chapter. This implies that the composition of the compounds is determined by the number of electron-pair covalent bonds which can be formed by the component atoms, or by the valency of the ions formed by these atoms. The law of constant proportions then finds its place as a corollary to the nature of the valence forces responsible for chemical combination. An examination of the whole range of chemical compounds shows, however, that this general principle is not sufficiently comprehensive to include every case. Thus, there are, on the one hand, certain classes of compounds, such as the nitrides and carbides of the heavy metals, or most of the intermetallic compounds, which defy interpretation in terms of any rational valency rules. Further, a closer examination shows that there are groups of compounds for which the law of constant proportions is no longer rigorously valid. The intermetallic compounds provide obvious examples of this type, but recent work has made it increasingly apparent that the phenomenon extends also to other classes of compounds—for example, the transition metal oxides and sulphides—which would not have been thought to deviate from strictly stoichiometric composition. Our knowledge of the possible binding forces between atoms has been sufficiently advanced by the quantum mechanical development of the electronic theory for us to be certain that these ‘exceptional’ classes of compounds must be capable of inclusion within the general scope of valency theory. In this chapter and the next, the essential features of these intermetallic and interstitial compounds (see below, p. 476) are described, and the theory of their nature is briefly and qualitatively discussed.¹

The study of intermetallic and interstitial compounds is essentially a study of the solid phase. Hence, they must necessarily

¹ For authoritative monographs on this subject, and on the theory of metals, see *The Structure of Metals and Alloys*, W. Hume-Rothery, Institute of Metals, 1936; *The Theory of the Properties of Metals and Alloys*, N. F. Mott and H. Jones, Clarendon Press, Oxford, 1936.

be discussed in the light of their crystal structure. Herein, indeed, lies the crux of the problem as to the validity of Dalton's and Proust's conceptions as to the fixity of chemical composition. Where a compound can exist in the form of discrete molecules—as a gas, a liquid, or in solution—the rigid stoichiometric laws must hold. In the cases to be considered in this chapter, however, the compounds can be said to exist only in the solid phase. In this sense, a compound can be defined only as a phase of definite and characteristic structure, which generally conforms closely to a simple chemical formula, but which may, in some cases, exist over a limited range of chemical composition. The application of this conception will become apparent in the following sections.

The systematic study of intermetallic compounds dates from the researches of Heycock and Neville, who established unambiguously for the first time the existence of compounds in the copper-tin system. In recent years, the methods of thermal analysis and micrographic examination have been supplemented, notably by the powerful methods of X-ray crystallography, which is especially valuable in that it provides a means of studying the important reactions and transformations which proceed in the solid phase. It affords, moreover, a more accurate method of fixing the range of existence, and therefore the formulæ of the phases formed, than is possible by the classical method.

Since about seventy of the elements are metals or semi-metals, the number of their possible combinations, in binary systems alone, is very large. Incomplete as the study of metal chemistry still is, the number and variety of the known compounds present a confusing picture. It is therefore necessary to look for such general principles as will enable as many as possible of the characteristic features to be related to basic chemical concepts.

The Elements of the Theory of Metals.—In applying the electronic theory of valency to pure metals and to intermetallic compounds, the suggestion was early made² that the cohesive forces; responsible for the characteristic properties of metals, were homopolar bonds of some type. Such a conception is not quite satisfactory, however, since intermetallic compounds share with pure metals those characteristic metallic optical and electrical properties which find their origin, as will be discussed, in the more or less free state of the valency electrons. Moreover, metals and intermetallic compounds commonly crystallize in structures wherein each atom is surrounded by a large number of equivalently placed neighbours; thus, in the hexagonal close-packed structure, and the face-centred cubic structure, each atom is the centre of a group of twelve equi-

² V. M. Goldschmidt, *Z. phys. Chem.*, 1928, 133, 397.

distant neighbours. This number far exceeds the number of available valency electrons, so that it is not possible to speak of any localized homopolar links. It is useful, before passing to the consideration of particular types of intermetallic systems, to consider briefly the elements of the modern theory of the metallic state. A detailed discussion of the theory of metals lies far beyond the scope of this book, but a qualitative consideration of the subject is of considerable value for the light it sheds not only upon intermetallic compound formation, but also on the characteristic electrical and magnetic properties of the metals.

The electrical and optical properties of metals require that metals should contain free electrons comparable in number with the number of atoms present. On the classical electromagnetic theory, the free electrons constitute an 'electron gas' which diffuses freely through the crystal lattice formed by the positive ions of the metallic element. Such a picture immediately encounters a fundamental difficulty, however, which was overcome only by the application of the newer quantum mechanical conceptions.³ The energy of the electrons in the electron gas would necessarily follow the Maxwell-Boltzmann distribution law, and O. W. Richardson's fundamental work on thermionics showed that the distribution of energy amongst the fastest electrons is, indeed, Maxwellian. On the other hand, if this were so, each electron must contribute a quantity $\frac{3}{2}kT$ to the specific heat (k = the Boltzmann constant) so that the total atomic heat would approach $\frac{3}{2}R$. In fact, however, the Dulong and Petit rule (*i.e.* that the atomic heat = $3R$) applies equally well to conductors and to insulators, which can have no free electrons. Thus, it appears either that the electrons contribute practically nothing to the specific heat, in contradiction to the electron gas conception, or else that there are far fewer free electrons than required by the optical theory.

The solution of the problem thus presented is associated with the work of Sommerfeld, Fermi and Bloch. As will be seen, it follows in essence directly from the application of the Pauli exclusion principle to the metallic electrons, whereby not more than two electrons, of opposed angular momentum, may occupy any one electronic state.

The underlying idea may be illustrated diagrammatically by considering the distribution of energy amongst the electrons in the atoms of, for example, the element neon. The neon atom contains ten electrons which, in a suitable electrical or magnetic field, are resolved into ten discrete energy levels. In an assemblage of neon

³ Useful reviews are given by Becker, *Z. Elektrochem.*, 1931, 37, 403, and U. Dehlinger, *ibid.*, 1932, 38, 148.

atoms, the 'population' $f(E)$ of each of these states may be plotted against the energy E of the state (Fig. 57). At the absolute zero of temperature, all the electrons are in the states of lowest possible energy, so that—bringing in the Pauli principle—the distribution follows the continuous line. Each state is then either completely filled, or else quite unoccupied; $f(E) = 0$ or 1 for each level. At temperatures high enough for the thermal energy to be comparable with the energy of excitation of the 'outermost' electrons, electrons may be promoted in some atoms of the assemblage from the 10th, 9th, etc., energy levels to the 11th, 12th, etc., (excited) levels. The statistical energy distribution is then represented by the dotted curve. Except where very large quanta of energy are available, the populations of the inner electronic states remain unchanged.

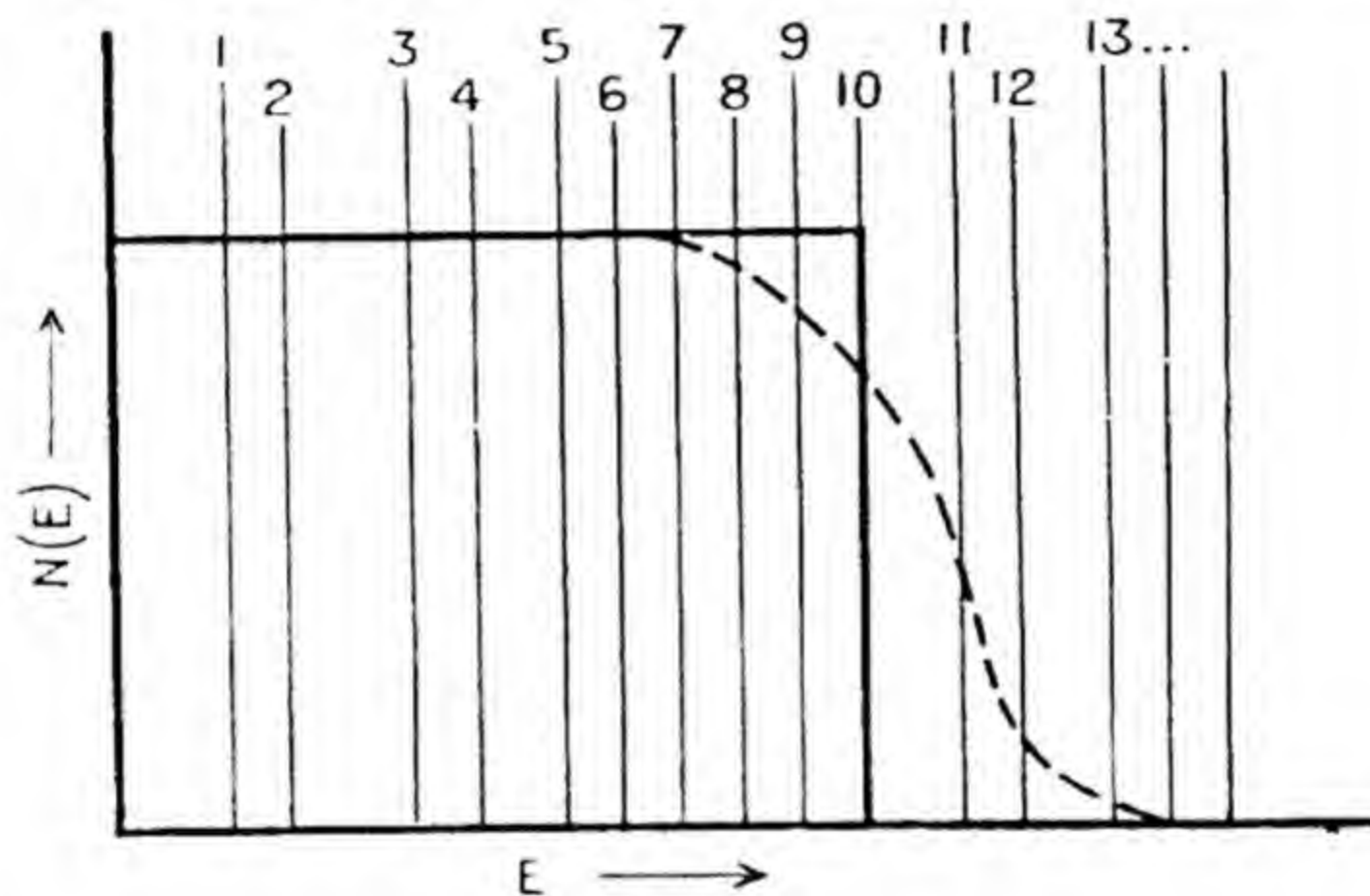


FIG. 57.

This picture may now be transferred to the metallic state. Just as, in the molecule of a compound, the electrons must strictly be referred to molecular orbitals, and not to the quantum levels originally occupied in the uncombined atoms, so a piece of metal—*e.g.* a single crystal—constitutes a giant molecule. The electrons are held in common by all the atoms contained in the unit, and have to be fitted into a very large, but discrete, number of energy states. Each of these, in accordance with the Pauli principle, holds two electrons. If the unit contains N electrons, then at the absolute zero, the first $\frac{N}{2}$ states will all be doubly occupied.

The electron is not merely particulate in nature, but has all the properties of a wave motion—as is shown, for example, by the diffraction of electrons at surfaces (Chap. V). Each possible

electronic state may therefore be described in terms of a wave function, which is a solution of the appropriate Schrödinger differential equation. If, then, as the simplest model, the potential within the metal be taken as uniformly zero, rising to a finite value at the boundary, the electron is represented by a stationary wave within the metallic crystal. It emerges from the solution of the wave equation that the wave-length of the electrons in the highest states is of the same order of magnitude as the distance between the atoms, and it follows that the energy of such electrons is several electron-volts in magnitude, greatly exceeding the thermal energy of an atom at room temperature ($3kT \sim 0.07$ e.v.). In accordance with the picture developed simply above, some of the electrons at temperatures above the absolute zero may be promoted to levels higher than the $\frac{N}{2}$ th, the energy distribution amongst

these electrons being then represented roughly by the dotted curve of Fig. 57, which—for the highest excited states—roughly follows the Maxwell-Boltzmann law. It is only these electrons, few at room temperature in comparison with the total number of electrons, which contribute to the heat capacity of the metal, so that the electronic contribution to the specific heat is inevitably small. The major part of the specific heat is expended in increasing the thermal energy of the atoms, so that metals conform to the Dulong and Petit rule.

In an actual metallic crystal, the potential field is not uniform, but periodic; the potential rises to a maximum at each positive ion, and is at a minimum between them. In such a case, the solution of the wave equation leads to a remarkable result. It emerges that the energy of the electrons cannot assume any value from zero to E_{max} , but there are certain discontinuities or bands of forbidden energies. Between these are bands of permitted energy values.

The origin of this allocation of energies lies in the wave nature of the electron, since—as was discussed in Chapter I—this implies that the electron density is not localized in a linear orbit; the radial distribution function falls off roughly exponentially to nothing, but has an appreciable value outside the 'classical' radius of the atom. For an s electron, the electron density distribution is spherically symmetrical. There is thus a certain overlap between the wave functions of the outer electrons of the closely adjacent atoms in a crystal lattice. The application of the Pauli principle brings as its consequence that whereas for an isolated atom the state of an electron (other than its spin) is uniquely particularized by its three quantum numbers, in the crystal each *quantum state* of the electrons

of the isolated atom is replaced by a *band* of permitted electronic states. As has been indicated, the breadth of the band depends on the amount of overlap between the wave functions, so that for the inner electrons of the constituent atoms the breadth of the band is extremely small—for the K electrons of sodium, for example, the spread of energies amounts to only about 2×10^{-19} e.v. The inner electrons—*e.g.* the K electrons—therefore have essentially the same energy that they would possess in the isolated atoms. For the outermost (valency) electrons, however, the overlap is great, so that the single valency electron of sodium, which has, in the isolated sodium atom, an energy defined completely by its *quantum state*

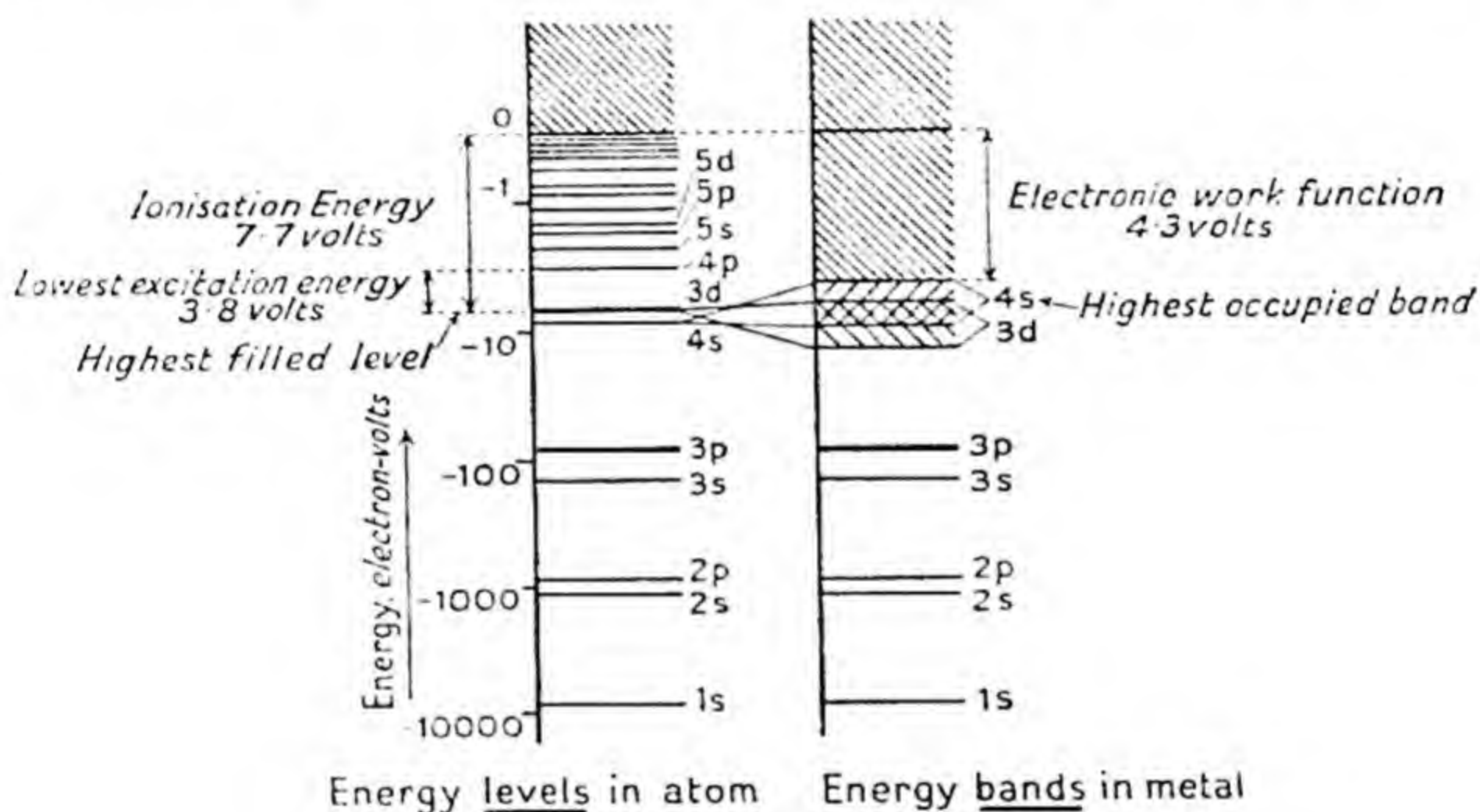


FIG. 58.

(3s), occupies in the crystal of metallic sodium some one of the many very closely-spaced energy values permitted within the corresponding 3s *energy band*. Within each energy band the permitted energies do not actually vary continuously, but except where assemblages of very few atoms are concerned, the spacing is extremely close. For crystals of finite size, the energy increment from one value to the next (within a band) is inappreciable. Each energy band corresponds, in principle, to one quantum level of an isolated atom, and the bands of forbidden energies correspond to the jumps in energy from one quantum state to the next. The relation between the energy levels in the isolated atom of copper, and in copper metal, are illustrated diagrammatically in Fig. 58.

Brillouin Zones.—The relationship between the permitted energies of electrons in a metal and the regular periodicity of the

crystal lattice through which they move can be expressed in another way. The wave mechanical nature of the electron implies that with an electron of energy E is associated a wave-length λ or, its reciprocal, a wave number k (cf. Chap. V, electron diffraction). Since the electron is moving in a certain direction, this is the direction of propagation of the corresponding wave packet; k is a vector quantity, therefore, and it characterizes both the energy and the direction of motion of the electron. For any particular direction of motion of electrons, there must be certain values of k corresponding to electron wave-lengths which satisfy the Bragg condition for reflection from certain planes within the crystal—exactly as in the diffraction of electrons impinging on the crystal lattice from without. Electrons with energies defined by these wave numbers cannot move freely through the crystal, so that these states are forbidden to electrons moving in that direction. The sum total of all the k states, differing in their energy and in their direction of propagation, which can be occupied without involving any large increment of energy, is known as a *Brillouin zone*. The relation of the Brillouin zones to the crystal structure cannot be discussed within the scope of this book; in brief, it follows from the way in which the limiting values of k have been defined that they are directly related to the crystallographer's theoretical concept of the reciprocal lattice of the crystal. Qualitatively, this means that for each type of structure the number of electrons per atom which may be inserted in the lowest Brillouin zone can be determined. If we conceive of electrons as being fed successively into a metallic crystal lattice, the electrons take up successively the electronic states within the first Brillouin zone. Eventually, when all these states are doubly occupied, the zone is full, and any more electrons added must enter a second Brillouin zone, separated from the first by an energy discontinuity.

Before the first zone is full, however, the theory shows that a stage is reached at which the energy of the electrons begins to increase rapidly as successive states are occupied. It is this point which proves to be significant for the understanding of the Hume-Rothery relations: it marks the point at which the tendency appears for the electrons to overflow into a second Brillouin zone if, as may happen, the lowest states of this zone have energies lower than those of the highest states in the first zone. Alternatively, the crystal lattice itself may undergo change into a structure providing more electronic states per atom within the first Brillouin zone. It is the latter phenomenon which brings about the characteristic succession of phases in binary alloys.

Metallic Conduction and Metallic Paramagnetism.—In

concluding this section it is of interest to discuss in the light of the theory outlined above two of the most characteristic properties of metals: their electrical conductivity and magnetic properties.

The conduction of electricity through metals is due to the movement of electrons through the crystal lattice, and is dependent on the possibility of such unidirectional movement under the electrical field gradient. The essential difference between conductors and insulators must therefore lie in the availability of the electrons for conduction. It is not that in insulators the electrons are intrinsically so much more tightly bound as to be unable to migrate, since such differences could not account for the enormous range covered by electrical conductivities—for example, the factor of 10^{24} between the conductivities of silver and fused silica. The essential is rather that it is only the electrons in singly occupied states—*i.e.* in incompletely filled bands—which can transport current. In a filled band the Pauli principle requires that the movement of any one electron must be compensated by the opposed movement of its partner in the level that it occupies, so that there is no nett transport of current.

It follows that an insulator is a solid in which every band that is occupied at all is completely filled. If, on the other hand, there is an incompletely filled Brillouin zone, the crystal must display metallic conductivity. The reason that the highest electrical conductivity is displayed by the univalent metals copper, silver and gold is then at once comprehensible. For N atoms, the first Brillouin zone of their cubic crystals is capable of holding $2N$ electrons, but actually contains only N valency electrons. The condition is that represented in Fig. 59A. The divalent metals, on the other hand, possess just enough electrons to fill the first Brillouin zone, so that if that zone alone were occupied, the metals would not conduct electricity. Since these metals are conductors, the second Brillouin zone must overlap the first (Fig. 59B), so that there are unpaired electrons available for conduction. Their number, however, is in general less than with univalent metals, so that the divalent metals (alkaline earths, zinc, cadmium, etc.) are not such good conductors as are copper, silver, gold or the alkalis.

The case of the diamond structure is of interest here. The theory shows that the first Brillouin zone can hold four electrons per atom. The diamond structure is, however, taken up by just those elements—carbon, silicon, germanium and grey tin—which have four valency electrons exterior to a closed electronic shell. The Brillouin zone is therefore just full, and since the next zone lies—especially for diamond and silicon—at considerably higher energies, these substances are perfect insulators, or semi-conductors

(case D, below). Similar considerations apply to certain intermetallic and metalloidal compounds— Mg_2Sn , Mg_2Pb , Mg_2Si , Mg_2Ge , Li_2S , Cu_2S , Be_2C . These all crystallize in the fluorspar structure, which should enable the first Brillouin zone to accommodate $8/3$ electrons per atom. Since this is the electron:atom ratio in all these compounds, the first Brillouin zone is just filled, and the crystalline substances should be insulators. They are, in fact, either insulators or semi-conductors. The molten compounds, however, in which the ordered crystal structure giving rise to the particular zone relationship is broken down, are good conductors.

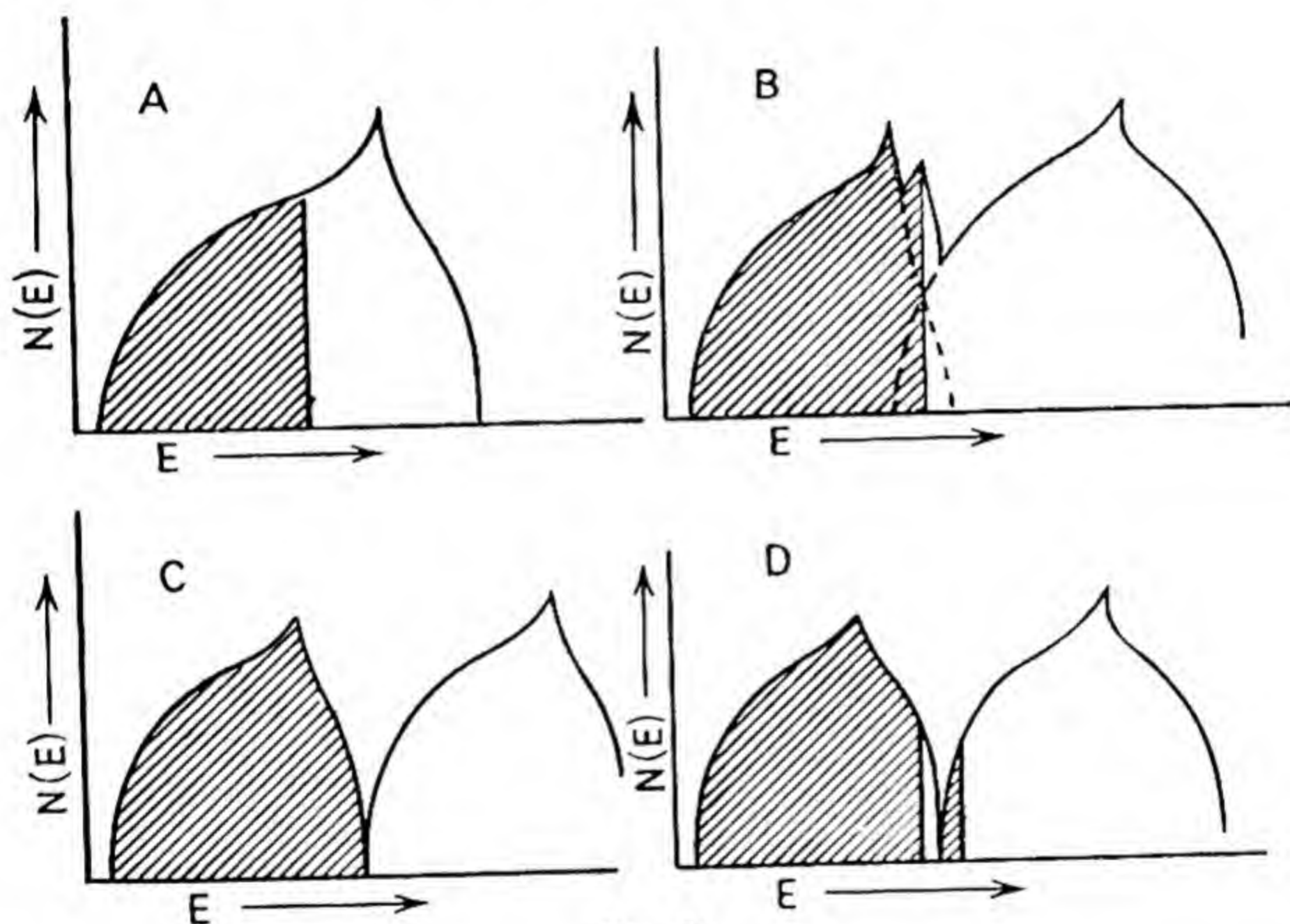


FIG. 59.

One more possible disposition of the Brillouin zones remains for consideration—that leading to the interesting property of semi-conductivity already referred to. If the first zone is just filled, while the second Brillouin zone, although not overlapping, lies very close to it, little energy is required to transport an electron across the gap into the second zone. Such an energy increment may be supplied as thermal energy, or by the absorption of light. At the absolute zero, all the electrons are in the lowest possible states (Fig. 59c); the first zone is completely filled and the substance is an insulator. At higher temperatures, the thermal energy can

promote some electrons to the next higher zone (Fig. 59D), with the result that the material shows a small conductivity which increases with rise of temperature. Where the absorption of a quantum of light may similarly promote an electron, the phenomenon of photo-conductivity is displayed, as in the cases of selenium and cuprous oxide.

The increase of conductivity with rise of temperature shown by semi-conductors is the opposite of the effect shown by metallic conductors. A perfect metallic lattice would have no resistance, since the resistance, according to the modern theory of metals, represents the scattering of electrons by imperfections in the crystal lattice. Since the thermal agitation of the atoms is largely contributive to this scattering, the effect must increase, and therefore the resistance must rise, as the temperature is raised. It is characteristic of metallic conductors that the specific resistance is a linear function of temperature.

Metallic Paramagnetism.—It has been explained in Chapter V that the magnetic susceptibility of the ions of the transition metals, which contain one or more unpaired electrons, is given by

$$\chi = \frac{\mu^2}{3kT}$$

where μ , the magnetic moment, is related to the total resultant spin, S , by the expression $\mu = \frac{eh}{2\pi mc} \sqrt{S(S+1)}$, in which e and m

represent the electronic charge and mass, respectively. Ionic paramagnetism therefore varies inversely with the temperature.

The alkali and alkaline earth metals, as also copper, silver, gold, magnesium, aluminium, the refractory carbides (*e.g.* TiC, VC) and nitrides, etc., possess a paramagnetism which is notable for its feebleness and its independence of temperature. Since the ionic cores of the metals, consisting only of completed shells, are diamagnetic, the paramagnetism must be attributed to the conduction electrons. Such magnetic properties follow from the theory of metals developed above.

Since each doubly occupied electronic state possesses zero resultant angular momentum, only the singly occupied states—*i.e.* the uppermost, unpaired electrons in incomplete Brillouin zones—can contribute to the paramagnetism. If the energy at the upper limit of the Brillouin zone is equivalent to the thermal energy at a temperature T_1 , and the maximum energy of the occupied states at the absolute zero corresponds to a temperature T_2 , then $T_1 - T_2$ is known as the Fermi limiting temperature, T_0 ; T_0 may be very large in magnitude—*e.g.* 6400° for silver. At any temperature,

T (T being small compared with T_0), approximately $\frac{T}{T_0}$ of the electrons occupy excited states, *i.e.* states with an energy greater than T_2 . Each of these electrons will contribute an amount $\frac{\mu_e^2}{3kT}$ to the total paramagnetism, where μ_e is the magnetic moment of the electron (*see above*). The total paramagnetism of the conduction electrons is then $\frac{\mu_e^2}{3kT} \cdot \frac{T}{T_0} \cdot N$, or $\frac{N\mu_e^2}{3kT_0}$, which is independent of temperature.

The transition metals are marked by a much larger paramagnetism which, in the first transition series, develops into ferromagnetism. This high paramagnetism, which is associated with the incomplete d shells of these atoms, is of interest in its bearing on the question of alloys and intermetallic compounds. It has already been mentioned that the nickel atom, for example, may possess in the lattice any one of the configurations $3d^84s^2$, $3d^94s$ or $3d^{10}$. It is clear that each electron promoted from the $3d$ to the $4s$ level leaves a 'positive hole' in the d shell, which contributes to the paramagnetism of the ion. In the case of nickel and palladium there is evidence that there are, statistically, about 0.6 unoccupied d states, or 0.6 electrons per atom in the s states.

In alloy systems of these metals, the magnetism may be reckoned directly from the resultant number of positive holes in the paramagnetic core. Thus, in copper-nickel alloys, the components form a complete series of mixed crystals. The progressive replacement of nickel ($Z = 28$) by copper ($Z = 29$) therefore consists essentially in the addition of electrons to the crystal lattice. These electrons go, for energetic reasons, for the most part into the d band, as long as there are any 'positive holes' in it to be filled up. With the composition 60 per cent Cu + 40 per cent Ni, 0.6 electron per atom has been added to the lattice. The d band should therefore be full at this point, and the paramagnetism should disappear. In accordance with this, the paramagnetism of nickel-copper alloys does fall linearly with increasing copper content, and may be extrapolated to zero at about 60 per cent of copper, although a complete neutralization of the original paramagnetism is not achieved in practice. Alloys of nickel with zinc ($Z = 30$), whereby two electrons are added per atom of zinc introduced, show a correspondingly steeper decline in susceptibility, whereas any increase in the number of 'positive holes' in the d band, by alloying with cobalt or iron, increases the paramagnetism.

It is of particular interest that the same reasoning can be applied

to the constitution of the palladium-hydrogen system. The paramagnetic susceptibility of 'palladium hydride' falls linearly with the amount of hydrogen absorbed, and finally disappears when the hydrogen taken up exceeds about 0.6 atom per atom of palladium. As already stated, there are known to be about 0.55–0.6 'positive holes' per atom in the d band of palladium. The change of susceptibility on absorption of hydrogen shows that, for each atom of hydrogen added, the electron goes into the d band, while the hydrogen enters the lattice as a hydrogen ion. A new light is thereby shed upon the old problem of the constitution of 'palladium hydride'; the question whether the compound is salt-like or homopolar in character is no longer relevant, and the absorption complex falls into place, on the evidence cited, as a typical alloy system.

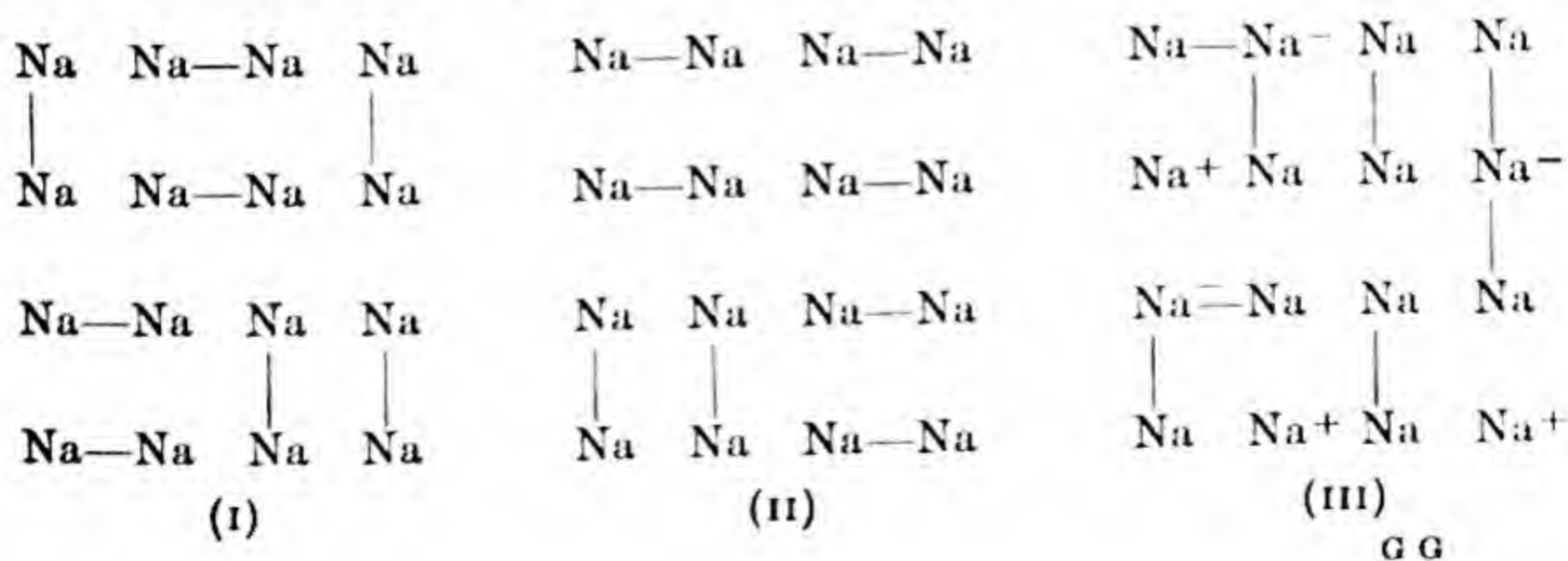
The Pauling Theory of Metals.—The Bloch-Sommerfeld theory just outlined can be compared with the molecular orbital treatment of simple molecules, in that the electrons are regarded as belonging collectively to all the atoms in the metallic crystal. In the discussion of simple molecules, an alternative approach—the Heitler-London concept of electron pair bonds and exchange forces—is often more useful. According to this, a polyatomic molecule can be constructed by considering only the overlap of wave functions (*i.e.* the sharing of electrons) between individual pairs of atoms, constituting a system of localized bonds, except in so far as resonance may be possible. Pauling⁴ has sought to apply the same treatment to the problems of the metallic state. In principle, both approaches should be applicable to any system of atoms and bonds, and should be complementary. In fact, the collective electron model lends itself far more to a precise treatment of the problems of metal physics, although a number of suggestive ideas have come out of Pauling's work.

As has been pointed out, the number of nearest neighbours (the co-ordination number) of every atom in a metal exceeds the number of valence electrons. Whilst this precludes the formation of localized bonds, Pauling supposes that resonance occurs, normal covalencies resonating between all the possible equivalent pairs of atoms. As was indicated earlier (Chapter III), the weighting of the canonical states is such that only bonds between directly neighbouring atoms are important. This implies that if an atom with z valence electrons has the co-ordination number N , each bond formed has an average *bond order* $n = z/N$. The alkali metals, with one valence electron, crystallizing in the body-centred cubic structure, give to each atom eight nearest neighbours and six others

⁴ *Phys. Review*, 1938, **54**, 899; *J. Amer. Chem. Soc.*, 1947, **69**, 542; *Proc. Roy. Soc.*, 1949, **A**, 196, 343.

almost as close, so that the bonds between the atoms are weak bonds, of order $n = \frac{1}{8}$ or less. The strength of the interatomic bonding directly determines the cohesive properties of the metal—*e.g.* its hardness and melting-point; furthermore, as is known from the lengths of the C—C bonds between singly, doubly and triply bonded carbon atoms, the effective diameter of a covalently bound atom varies directly with the bond order. That the alkali metals are soft, low melting and the least dense of the metals follows, accordingly, from the weakness of the bonds responsible for their cohesion. Pauling has sought, conversely, to work out the order of bonds, and therefore the distribution of electron density, from the observed interatomic distances in elements and alloys. However, the corrections which must be applied for the variation of atomic radius with co-ordination number and with bond order are purely empirical, so that it is not clear how much significance attaches to conclusions drawn from reasoning of this kind.

We may consider the resonance model for an alkali metal, such as sodium. The 3s valence electron of each atom can form a covalency with a neighbouring atom in the crystal lattice (I), and these bonds resonate around all equivalent pairs of atoms (II). In so far as only the one (3s) wave function is available for bonding no atom can form two bonds simultaneously, and the resonance switch has to be synchronous for all bonds. That sodium atoms can form covalencies by sharing 3s electrons is attested by the existence of the Na₂ molecule in sodium vapour; its energy levels and dissociation energy are well known from spectroscopic data. A comparison of its dissociation energy with the energy of sublimation of metallic sodium (per pair of Na atoms) gives a measure of the resonance energy of the bond system in the metal, and this proves to be larger than can be accounted for in terms of the number of distinguishable configurations allowed by synchronized resonance of bonds. It could be accounted for if resonance were completely random; this would bring with it the corollary that at any instant a proportion of the atoms must form two covalencies and, to do so, must accept



more electrons than can be accommodated in the 3s orbital (III). Pauling considers that the availability of an extra orbital for the acceptance of electrons in this manner is a necessary condition for the formation of a metallic structure. In the case of sodium, such a vacant orbital is available if the bonding arises from $[3s3p]$ hybrid orbitals, and not from the pure 3s orbital of the ground state of the atoms.

Pauling's idea that hybrid orbitals play a part in the metallic bond is important. It provides a connexion between the typical features of the general chemistry of the transition metals and their distinctive metallic properties. In each long period of the Periodic Classification the atomic radius decreases sharply from Group I to Group VI, is usually sensibly constant between Group VI and the coinage metals, and then increases. The hardness and melting-points follow a converse trend, the cohesion being at its maximum about Group VI. In Pauling's view, all nine s , p and d orbitals of the transition metals (*e.g.* $3d^54s4p^3$ in the first long period) are involved in the metallic bond, being divided into three sets: (i) a hybridized $[d^n s p^3]$ group of *bonding* orbitals, essentially similar to the $[d^2 s p^3]$ octohedral orbitals, with their strong bonding properties, used in co-ordination compounds; (ii) a group of m pure d orbitals, with no bonding properties, localized within the atom; and (iii) vacant *metallic* orbitals, $5 - (m + n)$ in number, which are necessary, as explained above, for metallic resonance to occur. Only the m *atomic* orbitals contribute to the paramagnetism of the transition metals, and Pauling has endeavoured to determine m from the magnetic properties of the transition metals in alloys. Both m and n may be fractional numbers (*e.g.* for iron Pauling assigns 5.78 bonding orbitals, 2.44 atomic orbitals and 0.78 metallic orbitals), which means only that the atoms must be present in two or more valence states. Other evidence for this has long been extant—*e.g.* the complex structure of α -manganese, and the atomic volumes and magnetic susceptibilities of the rare earth metals.⁵ The latter indicate that, in cerium, about 80 per cent of the atoms are present as Ce^{3+} and 20 per cent as Ce^{4+} ; in samarium, 20 per cent as Sm^{2+} and 80 per cent as Sm^{3+} . In the first transition series, the number of bonding electrons increases progressively from 1 in potassium to 5 in vanadium; with chromium the bonding orbitals are all singly occupied, and occupation of the atomic orbitals commences. The cohesion is then a maximum; paramagnetism appears and reaches its maximum value with iron, when all the atomic orbitals are singly occupied. The accession of additional electrons produces first, in cobalt and nickel, a decrease of paramagnetism

⁵ W. Klemm and H. Bommer, *Z. anorg. Chem.*, 1937, **231**, 138.

as singly occupied atomic orbitals become paired up, and then, commencing with copper, a decrease in the number of singly occupied orbitals available for bond formation. The metallic valencies of 4.5 and 3.5 so deduced for zinc and gallium respectively, though formally unorthodox, have been shown to be compatible with other data (*e.g.* on electron compounds, *see below*, p. 464). At this stage all *d* orbitals are filled; the properties of germanium involve only [*sp*³] hybrid orbitals, and metallic character diminishes sharply.

Pauling's interpretation of the constitution of observed metallic structures may be illustrated by two examples. Three possible electronic configurations might be assigned to the atom of *tin*, utilizing only 4*d*, 5*s* and 5*p* orbitals. These may be diagrammatically represented as SnA, SnB and SnC:

	4 <i>d</i>	5 <i>s</i>	5 <i>p</i>	Valency
SnA . .	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↓	↓ ↓ ↓	4
SnB . .	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑↓	↓ ↓	2
SnC . .	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑↓	↑↓	0

Atoms with the configuration SnA could form tetrahedral hybrid [*sp*³] orbitals, capable of forming four covalent bonds and building up a crystal lattice with the diamond structure. As the number of valence electrons exactly suffices for this, with no vacant metallic orbital, they could not form a structure with mobile electrons and metallic properties. This correctly describes the behaviour of silicon, with the [*3s3p*³] structure, and is roughly true for gray tin. Atoms with the configuration SnC would be non-bonding, but the bivalent tin atoms SnB would possess the vacant orbital requisite for metallic bonding. Pauling suggests that SnB predominates in white tin. This allotrope has a tetragonal structure of low co-ordination number, and not the crystal structure of a true metal. Each atom has four neighbours at a distance of 3.016 Å. in its own plane, and two at 3.175 Å. in adjacent planes. If—as Pauling has postulated without any clear justification—bonds of rational order are favoured in respect of stability, it may be inferred that each atom forms four bonds of order $\frac{1}{2}$ in the basal plane, and two bonds of order $\frac{1}{4}$ to atoms in the next plane of the structure. This implies an average valency of 2.5, due to the presence of configurations SnA and SnB in the ratio 1 : 3.

Zinc, although a hexagonal metal, is not ideal in structure; the

axial ratio $c/a = 1.856$, whereas that for close packing of atoms would be 1.633. Each zinc atom has, in consequence, six neighbours in the same plane, at 2.660 Å., and six in adjacent planes, at 2.907 Å. These bond lengths correspond to the formation of six bonds of order $\frac{1}{2}$ and six bonds of order $\frac{1}{4}$, as leading (in Pauling's view) to greater stability than the formation of twelve bonds of order $\frac{3}{8}$. The total valency, 4.5, is attributable to zinc atoms with the two configurations ZnA and ZnB. On the orthodox view only the configuration ZnC would be considered.

	3d	4s	4p	Valency
ZnA . .	↑↓ ↑↓ ↑↓ ↓ ↓	↓	↓ ↓ ↓	6
ZnB . .	↑↓ ↑↓ ↑↓ ↑↓ ↓	↓	↓ ↓	4
ZnC . .	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↓	↓	2

Pauling's theory is useful in its correlation of the metallic properties of the elements with the valence theory found adequate to treat general chemical problems. It provides a profitable, though essentially qualitative, way of looking at a number of problems in the chemistry of intermetallic compounds, and will be used from this standpoint from time to time in the following sections of this chapter.

Solid Solutions, Superstructures, and Intermetallic Compounds.—The criteria defining the status of an intermetallic compound are much less clear than for simple ionic compounds. This is, in part, a consequence of the mutual interchangeability of atoms in metals. Thus the atoms in a crystal of silver may be replaced by atoms of gold, forming a *mixed crystal* or *solid solution* of gold and silver. If the similarity between the atoms is close enough, as in the instance cited, miscibility may be complete; there is a complete range of solid solutions having any composition from 100 per cent Ag to 100 per cent Au, without the appearance of any new phase. In other cases, solid solutions may be stable only over a narrow range of compositions. One essential difference between metallic systems and ionic crystals may be emphasized. In an ionic compound MX, every ion is normally surrounded by ions of opposite charge, so that if an X^- ion were to be replaced by an M^+ ion, strong electrostatic repulsions would arise. In a solid solution of two metals A and B, both elements may be thought

of as present in the form of positive ions, embedded in an electron gas. Although the replacement of an atom of A by an atom of B may disturb the packing in the crystal lattice, or locally change the electron density distribution, no strong electrostatic effects are introduced.

The random, atom for atom replacement of one element by another gives rise to *substitutional* solid solutions, as represented schematically in Fig. 60 (c). Solid solutions can also be produced by incorporating atoms of the solute element between the atoms of the main constituent; in general this can happen only when the two species of atoms differ markedly in effective size. *Interstitial* solid solutions of this type (Fig. 60 (b)) are of importance in the compounds of boron, carbon, etc., with the heavy metals, as is discussed in the next chapter.

Where two metals do not form a continuous range of solid solutions, one or more *intermediate phases*, differing in crystal structure

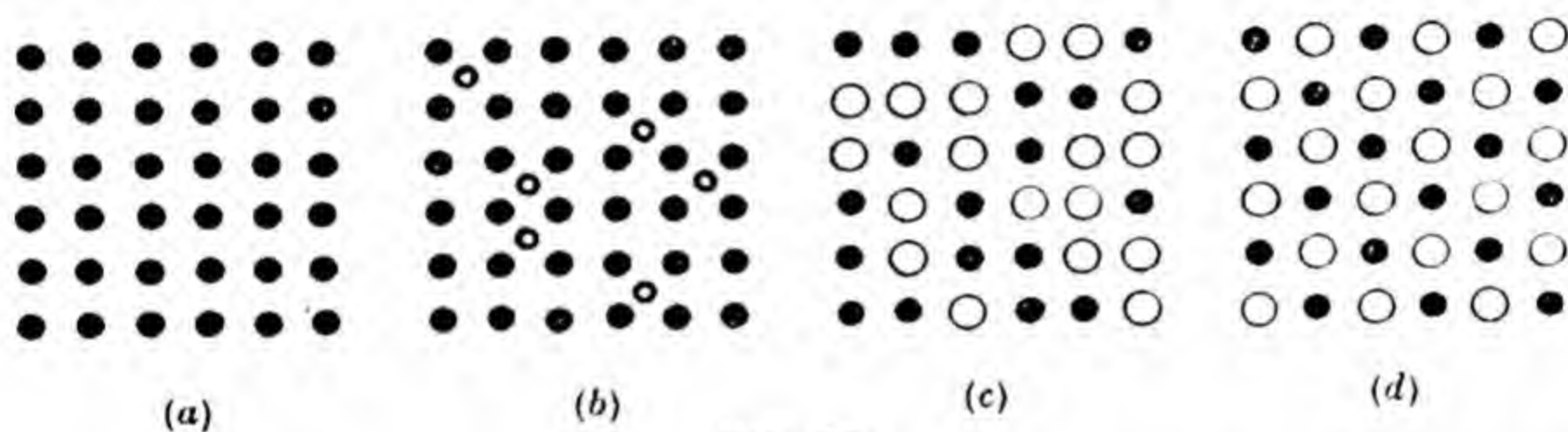


FIG. 60.

(a) Crystal lattice of a metal. (b) Interstitial solid solution. (c) Substitutional solid solution. (d) Superstructure.

from the component elements, may be formed. In these, as in simple solid solutions, it may be possible for the two sorts of atoms to be distributed quite at random over the lattice sites. This is the case, for example, in the body-centred cubic β -phase, CuZn, of the copper-zinc system, above 470° . When this is annealed at lower temperatures, an ordering process sets in; the copper and zinc atoms take up positions corresponding to the caesium chloride structure, so that each copper atom has only zinc atoms as nearest neighbours, and vice versa. A *superlattice* is thereby formed. The relation between the random structure and the superlattice is shown schematically by Fig. 60 (c) and (d). The order-disorder transition is a phase change of the second order, associated not with a latent heat, but with an enhanced specific heat, and taking place over a wide range of temperature. Such order-disorder changes are found to occur both in intermediate phases (as in β -brass) and in solid solutions of the elements (e.g. Cu₃Au).

Although the formation of substitutional solid solutions is of common occurrence, some intermetallic phases have compositions as uniquely limited as those of ionic compounds. In such cases, the assignment of a formula to the phase presents no difficulty. Where an intermediate phase exists over a range of compositions, it is still possible, in principle, to assign to it a chemical formula, based on the number of atoms of each sort which would be contained in the unit cell of the structure, if no mutual replacement or other defects of order occurred. Not only may this represent a considerable idealization of the analytical facts, in the case of phases with a wide range of stability, but the ideal composition may even lie outside the range of existence of the phase. Thus, in the sodium-lead system, the compound NaPb_3 actually exists as alloys having any composition in the range 27–35 atoms per cent of sodium; from 4 to 9 per cent of the lead atoms are invariably replaced by sodium.⁶ The stoichiometric compound cannot be obtained, and the maximum melting-point in the phase diagram is found for an alloy approximating to Na_2Pb_5 , the formula formerly assigned to the phase on the evidence of thermal analysis alone.

The chemistry of intermetallic compounds is but one section of a completely general theme—the mutual relationships of the chemical elements. That two elements should unite through metallic bonding, rather than by forming an ionic or simple covalent compound, is determined by the interplay of a number of factors, which vary continuously and regularly with the electronic structures of the atoms, as summarized in the Periodic Classification. At the one extreme, involving elements of widely differing electrochemical properties (ionization potentials, electron affinities), electron transference takes place, and ionic compounds result. If both elements have a high electron affinity, normal covalent compounds may be formed. Broadly speaking, metallic compounds are formed by the combination of atoms of low electron affinity.

It is of particular interest to enquire under what circumstances a transition of bond type occurs, and how the properties, structure and composition of the binary compounds of the elements are related to the electronic configurations of the components. It is convenient to distinguish three rough classes of elements: those of the B subgroups, with complete *d* levels, the very strongly electropositive metals 1–2 places following the inert gases, with very low ionization potentials (the alkalis, alkaline earths and also the rare earth elements), and the transition metals, truly metallic, but with partially filled *d* levels. Distinguishing these classes by the symbols *B*, *M* and *T* respectively, the chemical relationships between them

⁶ E. Zintl and A. Harder, *Z. phys. Chem.*, 1931, A, 154, 63.

might be systematically divided into systems of the types MM' , MB , MT , TT' , TB and BB' . Between these there is a continuous transition, and not all these classes present features of special interest for this chapter.

The Transition between Ionic and Metallic Compounds.—

Class MB.—The question whether the transition between one type of compound and the other is gradual or abrupt has been studied by Zintl⁷ and his co-workers, by examining the compounds formed by one and the same class M element with a series of elements stretching across the Periodic Table. The compounds formed between the alkali metals, lithium and sodium, and by magnesium, with the elements of the B sub-groups are summarized in Tables 1 and 2.

It is evident that, combined with a highly electropositive element, the elements standing from one to three places before an inert gas give rise to compounds formulated according to the normal valency rules, and having the structures typical of salt-like compounds. The elements five to seven places from the inert gases, on the other hand, form a multiplicity of compounds. Between these two classes, the elements of Group IVB constitute some measure of transition, since although many of the compounds are formulated according to the valency rules (Mg_2Pb , Li_4Sn), even these have the physical properties of poor metals. Nevertheless, as will be seen later, there is some evidence for some measure of heteropolar character even in the alloy phases formed by the elements of the earlier B sub-groups.

Tables 1 and 2 emphasize that in the intermetallic compounds there is no necessary and simple connexion between the formulæ and any one of the variables (*e.g.* the valency) characterizing the components. There is evidence for the frequent recurrence of certain structures, some relatively simple, such as the MB_3 structure of $NaPb_3$, $CaPb_3$, $BaPb_3$, $LaPb_3$, others complex, which themselves determine the formulæ of the compounds, especially when the relative sizes of the atoms fulfil certain geometrical conditions. Thus, with atoms X , Y such that $r_X = \text{about } 1.25r_Y$, it is frequently found that a compound XY_2 exists, having a structure typical of one or other of the so-called Laves phases.⁸ Some compounds with this structure are marked with an asterisk in Tables 1, 2, 3 and 4. The relative electropositivity and the valency of the atoms X and Y are of subordinate importance (though at least one element is of, or close to, the class M), and compounds differing as widely as KNa_2 , KBi_2 and ZrW_2 are all Laves phases. No common factor

⁷ *Angew. Chem.*, 1939, 52, 1. See also the Zintl Memorial Address, *Ber.*, 1942, 75, A, 45.

⁸ G. E. R. Schulze, *Z. Elektrochem.*, 1939, 45, 869.

Table 1

Compounds of Lithium and Sodium with B Sub-group Elements

	<i>I_B</i>	<i>II_B</i>	<i>III_B</i>	<i>IV_B</i>	<i>V_B</i>	<i>VI_B</i>	<i>VII_B</i>
Li		LiZn Li ₂ Zn ₃ LiZn ₂ Li ₂ Zn ₅ LiZn ₄	LiGa		Li ₃ As	Li ₂ Se	LiBr
	Li ₃ Ag LiAg	Li ₃ Cd LiCd LiCd ₃	LiIn	Li ₄ Sn Li ₇ Sn ₂ Li ₅ Sn ₂ Li ₂ Sn LiSn LiSn ₂	Li ₃ Sb	Li ₂ Te	LiI
		Li ₈ Hg Li ₃ Hg Li ₂ Hg LiHg LiHg ₂ LiHg ₃	Li ₄ Tl Li ₃ Tl Li ₅ Tl ₂ Li ₂ Tl LiTl	Li ₄ Pb Li ₇ Pb ₂ Li ₃ Pb Li ₅ Pb ₂ LiPb	Li ₃ Bi		
Na		NaZn ₄ NaZn ₁₃		NaGe	Na ₃ As	Na ₂ Se	NaBr
		NaCd ₂ NaCd ₅	NaIn	Na ₁₅ Sn ₄ Na ₂ Sn Na ₄ Sn ₃ NaSn NaSn ₂	Na ₃ Sb	Na ₂ Te	NaI
	Na ₂ Au NaAu ₂ *	Na ₃ Hg Na ₅ Hg ₂ Na ₃ Hg ₂ NaHg Na ₇ Hg ₈ NaHg ₂ NaHg ₄	Na ₆ Tl Na ₂ Tl NaTl	Na ₁₅ Pb ₄ Na ₅ Pb ₂ Na ₂ Pb NaPb NaPb ₃			
ALLOY TYPE STRUCTURES					IONIC TYPE STRUCTURES		
					LaF ₃ or BiF ₃	CaF ₂	NaCl

Table 2

Transition from Salt Type to Intermetallic Compound in Magnesium Compounds

I _B	II _B	III _B	IV _B	V _B	VI _B	VII _B
		Al ₃ Mg ₂ Al ₁₂ Mg ₁₇	Mg ₂ Si	Mg ₃ P ₂	MgS	MgCl ₂
Mg ₂ Cu MgCu ₂ *	MgZn MgZn ₂ * Mg ₂ Zn ₁₁	Mg ₅ Ga ₂ Mg ₂ Ga MgGa MgGa ₂	Mg ₂ Ge	Mg ₃ As ₂	MgSe	MgBr ₂
Mg ₃ Ag MgAg	Mg ₃ Cd MgCd ₃	Mg ₅ In ₂ Mg ₂ In MgIn MgIn ₃	Mg ₂ Sn	Mg ₃ Sb ₂	MgTe	MgI ₂
Mg ₃ Au Mg ₅ Au ₂ Mg ₂ Au MgAu	Mg ₃ Hg Mg ₅ Hg ₂ Mg ₂ Hg Mg ₅ Hg ₃ MgHg MgHg ₂	Mg ₅ Tl ₂ Mg ₂ Tl MgTl	Mg ₂ Pb	Mg ₃ Bi ₂		
ALLOY TYPE STRUCTURES			SALT-LIKE STRUCTURES			
			CaF ₂	Me ₂ O ₃	NaCl or ZnO	TiO ₂ or layer

except the geometric is discernible here. On the other hand, some intermetallic phases have complex structures, with many atoms in the unit cell—*e.g.* Mg₁₇Al₁₂, with 58 atoms in the unit cell, having the same structure as α -Mn and α -Cr. The formation of phases such as this can clearly not be explained on a geometrical basis, and there is, in fact, no easy generalization covering the combining proportions of the metals with each other.

Compounds of base metals with each other. Class MM'.—Tables 3 and 4 illustrate the behaviour of pairs of metals of similar, high electropositivity. In any one family, the factor of atomic size is likely to determine the phases formed; in the relations of Group I metals with Group II metals, the electron : atom ratio is probably more important. Where, as with K-Rb, K-Cs, the radii of the atoms differ by not more than about 10–15 per cent, solid solution

occurs. The radius ratio $r_{\text{Na}} : r_{\text{K}}$ is about 1.25. This is too large to permit of appreciable miscibility in the solid state, but appropriate for the formation of a Laves phase. Lithium occupies a somewhat

Table 3

	<i>Na</i>	<i>K</i>	<i>Rb</i>	<i>Cs</i>	<i>Mg</i>	<i>Ca</i>	<i>Al</i>
Li	p. misc. s.s.	not misc. —	not misc. —	not misc. —	misc. LiMg ₂	misc. Li ₂ Ca*	misc. Li ₂ Al LiAl
Na		misc. Na ₂ K*	misc. —	misc. Na ₂ Cs	p. misc. —	p. misc. —	p. misc. —
K			misc. s.s.	misc. s.s.	p. misc. —	not misc. —	p. misc. —

Misc. = miscible, *p. misc.* = partly miscible, *not misc.* = immiscible in liquid state.

s.s. = form solid solutions.

Table 4

	<i>Ca</i>	<i>Sr</i>	<i>Ba</i>	<i>Al</i>	<i>La</i>
Mg	Mg ₂ Ca*	Mg ₃ Sr Mg ₄ Sr Mg ₂ Sr*	Mg ₃ Ba Mg ₄ Ba Mg ₂ Ba*	Mg ₁₁ Al ₁₂ MgAl Mg ₂ Al ₃	Mg ₃ La Mg ₂ La* MgLa MgLa ₄
Ca		solid soln	solid soln	CaAl ₂ * CaAl ₃	
Sr			solid soln	SrAl SrAl ₃	
Al					Al ₄ La Al ₂ La* AlLa

anomalous position, in being immiscible with the other alkalis, even in the liquid state. The faculty of the bivalent and trivalent elements for combining amongst themselves is to be contrasted with

the behaviour of the alkalis. It can be correlated with their higher melting-points (stronger cohesive forces) and lower electrical conductivity, as the consequence of their higher ratio of electrons : atoms and the stronger interaction between the multivalent atoms and the surrounding electron gas.

Classes TM, TT', TB.—Table 5 shows the compounds formed by

Table 5

	IA	IIA	IIIA	IVA	VA	VIA	VIIA	
Cu	—	Cu ₄ Ca CuCa ₄	CuLa Cu ₂ La Cu ₃ La Cu ₄ La	Cu ₃ Ti CuTi ₂	—	—	—	—
Zn	KZn ₁₃	ZnCa ₄ ZnCa Zn ₄ Ca Zn ₁₀ Ca	—	ZnTi Zn ₃ Ti	—	—	Zn ₃ Mn Zn ₇ Mn	Fe ₅ Zn ₂₁ FeZn ₇
Fe	—	—	Al ₃ Fe Al ₅ Fe ₂ Al ₂ Fe AlFe AlFe ₃	Fe ₂ Ti FeTi	s.s. FeV	s.s. FeCr	s.s. FeMn	—
			IB	IIB	IIIB	IVB	Vn	VI n
Cu	Cu ₂ Rh CuRh CuRh ₂	Cu ₃ Pd CuPd	—	CuZn ₃ Cu ₂ Zn ₃ Cu ₅ Zn ₈ CuZn	Cu ₉ Ga ₄ Cu ₃ Ga	Cu ₆ Sn ₃ Cu ₃ Sn Cu ₃₁ Sn ₈ Cu ₅ Sn	Cu ₃ As	Cu ₂ Se CuSe
Zn	Co ₅ Zn ₂₁ CoZn	Ni ₅ Zn ₂₁ NiZn	Zn ₃ Cu Zn ₃ Cu ₂ Zn ₈ Cu ₅ ZnCu	—	—	—	Zn ₃ As ₂ ZnAs ₂	ZnSe
Fe	s.s.	s.s. FeNi ₂	—	Zn ₇ Fe Zn ₂₁ Fe ₆ Zn ₁₃ Fe	—	Fe ₂ Sn FeSn FeSn ₂	Fe ₂ As Fe ₃ As ₂ FeAs FeAs ₂	FeSe

iron (with partly filled *d* levels), copper (at the end of the transition series) and zinc, for comparison with Tables 3 and 4. It is characteristic of the transition metals proper that they form neither compounds nor solid solutions with the alkalis and alkaline earths, but are completely miscible with the elements in the centre of the long periods. Superstructure phases may be formed from these solid

solutions, and the phases FeV , FeCr , FeNi_2 are in this category. In terms of Pauling's theory, the valency is practically constant between vanadium or chromium and nickel, only a change in the population of the unshared atomic orbitals taking place. Since, in addition, the atomic radius changes but little, this sequence of elements fulfils the conditions requisite for facile solid solution.

Tables 1, 2 and 3 show that it is characteristic of the metals of the B sub-groups that they form a large number of compounds, both with the most electropositive metals and with the transition metals. With the former, the compounds tend to have relatively narrow ranges of composition. In their compounds with each other (type BB') and with the transition metals it is common for the intermediate phases to possess very wide ranges of homogeneity. Amongst the intermetallic compounds in the last class (type TB) are a number for which, as was first perceived by Hume-Rothery, the formulæ and structures are determined by the ratio of the number of valency electrons to the total number of atoms of both kinds. The principle involved here is different from that determining the composition of heteropolar compounds, and the importance of these 'electron compounds' is such as to warrant a more detailed consideration.

The Succession of Hume-Rothery Phases.—It is characteristic of a number of these TB alloy systems, and especially those of copper and silver with aluminium and the metals of Groups IIB and IIIB, that whilst the intermediate phases differ widely in *composition* from one system to another, certain *structures* are encountered, in numerous systems and in the same sequence, when the composition of the alloys is progressively changed.

If two metals of different valency—*e.g.* copper with valency one, and zinc with valency two—form an extensive range of solid solutions, the effect of changing the composition of the system, replacing copper atoms by zinc atoms, is essentially to change the concentration of valency electrons. The solid solution phase may tolerate within a certain limit changes in the ratio of valence electrons to atoms. If this limit is exceeded, another structure may become more stable, and a new phase appears. In the alloy systems conforming with Hume-Rothery's rules, when the metal of higher valency is added in increasing proportions to the metal of lower valency there is formed a succession of intermediate phases, notably certain phases having the same crystal structure and recurring in many binary systems.

This succession of phases may be illustrated by the copper-zinc system (Fig. 61). Pure copper has a face-centred cubic structure; on adding to it increasing amounts of zinc, the zinc atoms at first

merely replace copper atoms in the face-centred cubic lattice. When the limit of this simple solid solution is reached, a new phase,

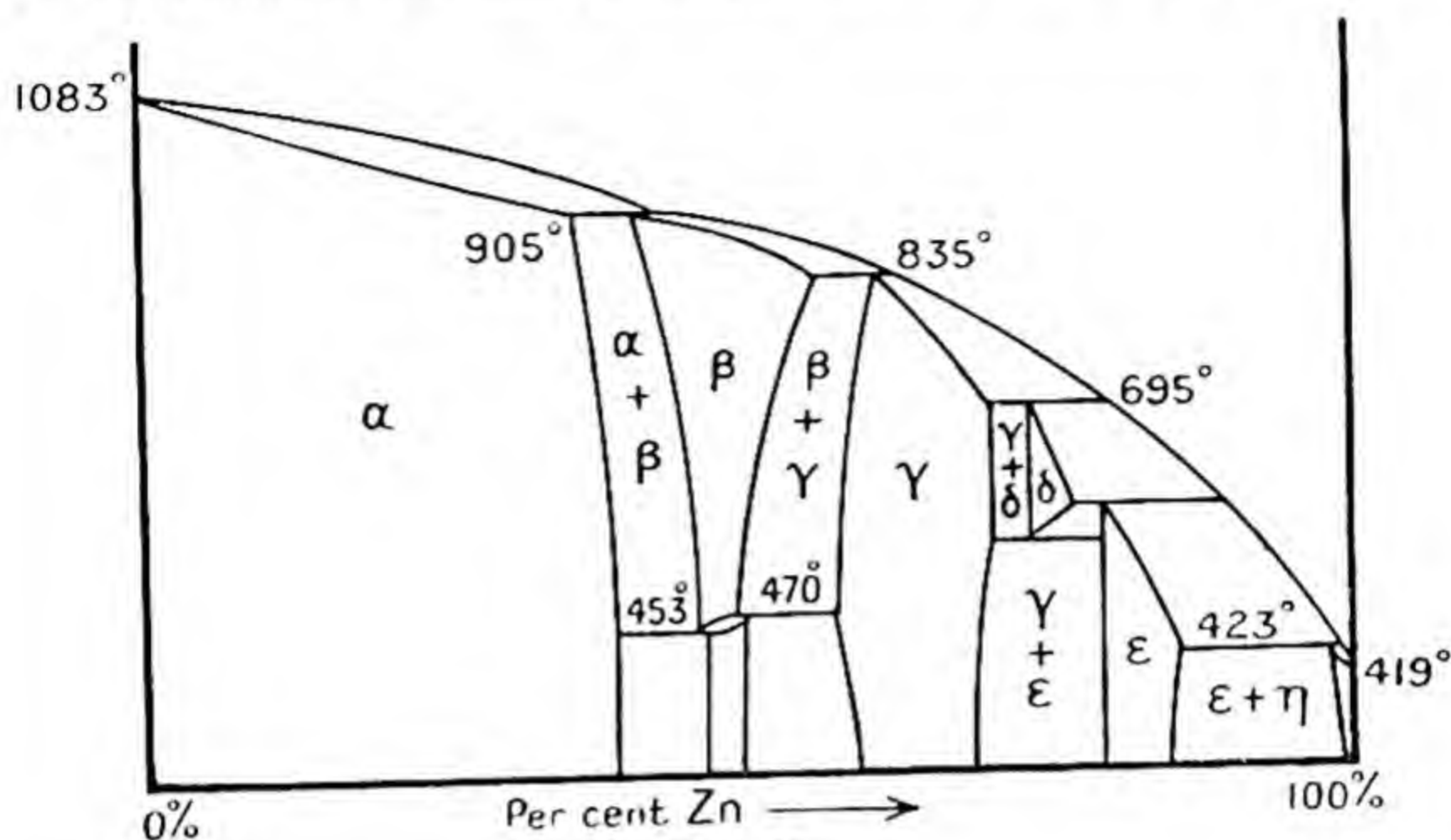


FIG. 61.

with a body-centred cubic structure, known as β -brass, appears. This, in turn, gives place to a so-called γ -phase, which is again based upon the cubic system, but which possesses a complicated

Table 6

β -structures		γ -structures	ϵ -structures
β -brass	β -manganese		
CuZn . .		Cu_5Zn_8	CuZn_3
AgZn . .		Ag_5Zn_8	AgZn_3
AuZn . .		Au_5Zn_8	AuZn_3
AgCd . .			AgCd_3
Cu_3Al . .		Cu_9Al_4	
	Ag_3Al		Ag_5Al_3
Cu_6Sn . .		$\text{Cu}_{31}\text{Sn}_8$	Cu_3Sn
	Cu_5Si	$\text{Cu}_{31}\text{Si}_8$	Cu_3Si
CoAl . .		$\text{Co}_5\text{Zn}_{21}$	
	CoZn_3	$\text{Ni}_5\text{Zn}_{21}$	
		$\text{Pt}_5\text{Zn}_{21}$	
		$\text{Rh}_5\text{Zn}_{21}$	
FeAl . .			
NiAl . .			
		$\text{Na}_{31}\text{Pb}_8$	

structure. The next phase to appear, the ϵ -phase, has the hexagonal close-packed structure.

This succession of face-centred cubic \rightarrow body-centred cubic (β -phase) \rightarrow γ -phase \rightarrow close-packed hexagonal (ϵ -phase) is of frequent occurrence. In some cases (see Table 6) the β -brass body-centred cubic structure is replaced by a related, but more complex, cubic phase, known as the β -manganese structure. The compositions assigned to the intermetallic compounds in these binary alloy systems are rationalized formulæ. The intermediate phases have a range of homogeneity in every case, and for certain of them this is extensive.

The Hume-Rothery Rules.—While the composition of the successive phases differs widely from one system to another, the ratio of the total number of valency electrons to the total number of atoms is a constant for each type of phase.⁹ For the β -brass and β -manganese structures, this ratio is 3 : 2. As may be seen from the above table, this ratio is attained in all the copper alloys listed if copper contributes one valency electron. Thus, for CuZn (2 atoms) we have $1 + 2 = 3$ electrons; for Cu_5Si (6 atoms), $5 + 4 = 9$ electrons; for Cu_3Al or Ag_3Al (4 atoms), 6 electrons.

In the γ -phase, the ratio is 21 : 13 throughout. It is especially interesting to observe that the tendency to acquire the characteristic γ -structure may override the normally expected ratios of combination. Thus, in the Na-Pb system, where the formation of a plumbide, Na_4Pb , might be expected, the compound actually formed is $\text{Na}_{31}\text{Pb}_8$, in conformity with the Hume-Rothery rule.¹⁰ The formation of a γ -structure where the electron : atom ratio reaches 21 : 13 is observed even in ternary alloys, so that in the Cu-Al-Zn system, the alloys $\text{Cu}_6\text{Zn}_6\text{Al}$, $\text{Cu}_8\text{Zn}_2\text{Al}_3$ constitute γ -phases. A similar constant electron : atom ratio of 7 : 4 applies to the close-packed hexagonal ϵ -phase.

It will be observed that the Hume-Rothery rules apply to the β - and γ -phase compounds of the transition metals Fe, Co, Ni, Pd, etc., only if these elements contribute no valency electrons to the alloy structure.¹¹ This behaviour in alloys may be correlated with the manner in which just these same elements display zero valency in the metal carbonyls, and it may be explained quantitatively in terms of their atomic structure.

⁹ Hume-Rothery, *J. Inst. Metals*, 1926, 35, 295; *Phil. Mag.*, 1927, [vii], 3, 301; A. F. Westgren and G. Phragmén, *Trans. Faraday Soc.*, 1929, 25, 379.

¹⁰ C. W. Stillwell and W. K. Robinson, *J. Amer. Chem. Soc.*, 1933, 55, 127.

¹¹ W. Ekman, *Z. physikal. Chem.*, 1931, B, 12, 57; Westgren and Phragmén, *loc. cit.*, Ref. 9.

The transition metal atoms are those in which (considering the first transition series) the $3d$ quantum level is approaching completion. Thus, for nickel there are three possible electronic configurations which, omitting completed levels, may be symbolized as $3d^8 4s^2$, $3d^9 4s$ and $3d^{10}$; in these the nickel atom possesses two, one or no effective valency electrons, respectively. The ground state of the atom is $3d^9 4s$, but the configuration $3d^{10}$ lies at only about 1.25 electron-volts higher energy. The energy of binding of a nickel atom in the metallic lattice is of the order of 4 electron-volts, so that it is not unreasonable that the atom should enter in the $3d^{10}$ configuration, without contributing any valency electrons to the structure.

However, it appears that this arbitrary assumption is not required if the ratios are based on Pauling's valencies. These also furnish a self-consistent set of electron : atom ratios for the Hume-Rothery phases.

It has been found possible, on the basis of the quantum theory of metals, to justify the valence electron : atom ratios, which were advanced as empirical relations. Reference was made in an earlier paragraph to the relatively large increment of energy per electron added to a nearly full Brillouin zone. For the face-centred cubic lattice, *i.e.* the α -phase in alloy systems, the calculated critical electron : atom ratio should be reached when the first Brillouin zone contains 1.362 electrons per atom; for the closely related β -brass and β -manganese structures, $n_c = 1.480$ electrons per atom; for the complicated γ -phase, $n_c = 1.538$, and for the ϵ -phase, $n_c = 1.75$ electrons per atom. The Hume-Rothery ratios, as discussed in a previous paragraph, are 1.50, 1.615 and 1.75 electrons per atom for the β -, γ -, and ϵ -phases, respectively. These ratios (3 : 2, 21 : 13 and 7 : 4) are, of course, actually rationalized to give the nearest integral figures consistent with the various systems; each phase actually covers a certain range of compositions, since solid solutions are formed. Where the phase boundaries narrow until they meet, as is the case in some systems, a more precise meaning may be attached to the electron : atom ratio. Values found for a few systems, compared with the theoretical n_c values for the corresponding structures, are listed in Table 7.

It may be seen that the scheme developed above, due largely to the work of H. Jones, affords a consistent picture of the transformations.

Zintl Phases.—The work of Zintl and his school has shown that alloys of the most highly electropositive metals with metals of the B sub-groups (including gold also) afford suggestive evidence of mixed metallic and heteropolar character. The fact that a

Table 7

	Maximum Electron Ratio in α -phase	Lower Limit of β -phase	Boundaries of γ -phase
n_c theoretical	1.362	1.480	1.538
Hume-Rothery ratio	—	1.50	1.615
Cu-Zn	1.384	1.48	1.58–1.66
Cu-Sn	1.270	1.49	1.67–1.67
Ag-Cd	1.425	1.50	1.59–1.63
Cu-Si	1.420	1.49	—
Ag-Zn	1.378	—	1.58–1.63
Cu-Al	1.408	1.48	1.63–1.77

number of the compounds of the simple type MB (e.g. LiHg, MgTl, CaTl) have the caesium chloride structure is not, in itself, necessarily significant, for although this is a structure typical of ionic compounds it is assumed also by the superstructure phases TT' of the transition metals. Whether purely metallic or partly ionic, the interatomic distances in this structure are determined jointly by the sizes of the atoms M and B .

There are, however, certain alloys of the same formal composition MB , and others of the type MB_{13} , which introduce a new principle, in that the dimensions depend solely on the nature of the atom B . It may be inferred that the B atoms build up some structural framework into which the M atoms fit, their size being of secondary importance.

The first group of compounds may be exemplified by LiAl, NaTl, LiZn, LiCd, having a simple structure with the M and B atoms occupying alternate sites on a body-centred cubic lattice. Each atom has four neighbours of each kind, and the two sorts of atom have apparently equal radii. In this sodium thallide structure the Na atoms and Tl atoms each lie as in the crystal lattice of diamond, or gray tin, and as has been indicated, it can reasonably be inferred, that the thallium atoms are bonded together to form a three-dimensional diamond type network. The alkali atoms fit into the interstices of this, but their apparent radius is determined by the thallium framework. The diamond structure involves four bonds per atom; if there were complete transference of an electron, so that the structure were built up from Na^+ and Tl^- ions, each of the latter would have the four electrons needed to form four normal covalencies. It is, perhaps, not necessary that electron transfer should be complete; there may be some metallic bonding between Na-Tl, with non-integral Tl-Tl bonds also. In LiCd and LiZn,

which are described as intensely coloured compounds, the three-dimensional framework involves, at most, three electrons per Zn^- or Cd^- ion, resonating amongst four bonds. It is not clear whether the compounds have any marked metallic character. The compounds $(\text{Na}, \text{K}, \text{Ca}, \text{Sr}, \text{Ba})\text{Zn}_{13}$ and $(\text{K}, \text{Rb} \text{ or } \text{Cs})\text{Cd}_{13}$ have complicated structures, but illustrate Zintl's viewpoint strikingly, since the dimensions of the cubic unit cell change only from 12.27 Å. to 12.33 Å. in passing from NaZn_{13} to BaZn_{13} , a substitution involving a much larger atom and (if bonding were purely metallic) the operation of stronger forces by the bivalent atom.

The same structural plan can be discerned in other compounds also. Thus CaZn_2 contains hexagonal sheets of zinc atoms, somewhat distorted from a pseudo-graphite structure by the insertion of calcium atoms between them. The structure suggests that it is built up essentially from Ca^{2+} and Zn^- ions; the latter, with three electrons, then build up a system of $[sp^2]$ trigonal bonds. In all these compounds the operative factor is the combination of a metal of extreme electropositivity with an element having sufficient electron affinity to form strong covalent bonds. The metals forming the framework of Zintl phases are also those which form organometallic compounds.

That the part played by heteropolar forces in alloys is not negligible has been borne out by measurements of electrolytic transference. Although the metallic electrons, because of their high concentration and mobility, are necessarily the main current carriers, a certain concentration of ions will be present in a solid with partially ionic binding. If the temperature is high enough to permit of diffusion, the ions will migrate also during the passage of an electric current. Their transference number will depend on the effective concentration of atoms in ionic form, and on the relative mobility of ions and electrons. An alloy of mixed valence type might therefore have the properties of a solid electrolyte superimposed on the quantitatively predominating electronic conduction. Even in a purely metallic system, the electron gas and the positively charged atomic cores should both contribute to the passage of current, and if, in a binary alloy, the mobilities of the two species of atoms differs markedly, some changes in concentration should be observable. This is, indeed, the case, as has been found for the Pd-H^{12} and $^*\text{Fe-C}^{13}$ systems, and in the truly metallic systems Pd-Au and Cu-Au^{14} also, but the apparent ionic transference numbers are excessively small. In more polar alloys, however,

¹² A. Coehn and W. Specht, *Z. Physik*, 1930, 62, 1.

¹³ W. Seith and O. Kubaschewski, *Z. Elektrochem.*, 1935, 41, 551.

¹⁴ W. Jost and R. Linke, *Z. phys. Chem.*, 1935, B 29, 127.

there should be migration of ions in both directions, and any ionic component of the transport of current may be more readily observed. Thus in Mg_3Bi_2 at 700°C . about 0.1 per cent of the current is transported by ions, the bismuth being transported to the anode.¹⁵ The ionic transport number varies with the composition of the phase, and is a maximum for the stoichiometric compound, which has the minimum conductivity also. In view of the disparity between the mobilities of electrons and of massive ions, this ionic transference number indicates that a very appreciable proportion of the electrons must be trapped in the form of Bi^{n-} ions (n is not necessarily 3), instead of being in the form of freely mobile metallic electrons. On certain assumptions, Kubaschewski calculates that the binding forces must be 80–90 per cent ionic in this compound. Few intermetallic phases have as yet been investigated from this standpoint. Kubaschewski and Reinartz have, however, found evidence for a perceptible ionic component in the conduction of the Hume-Rothery β -phase Cu_3Al .

Polyanionic Compounds of Lead, Tin and Antimony.—A link between the intermetallic compounds, in which the usual valency rules do not apply, and the normal type of chemical combination is provided by an interesting group of compounds investigated by Zintl and his co-workers.¹⁶ These polyanionic salts serve also as a link with the polysulphides and polyiodides, the constitution of which is still little known.

It was first observed by Joannis, and later confirmed by Kraus, Bergström and Smyth,¹⁷ that a solution of sodium in liquid ammonia could dissolve metallic lead, forming a conducting solution. These authors rightly surmised that a compound resembling a polysulphide was formed, but the elucidation of the composition of the substance awaited the application of an elegant experimental technique developed by Zintl. This turns upon a second method of formation of the polyplumbides—*viz.* the action of an excess of sodium on a solution of lead iodide in liquid ammonia. The course of the reaction was studied by conductometric and potentiometric titrations in liquid ammonia solution, and it was established that not only with lead, but also with the other metals of Groups IVB, VB and VIB—*i.e.* with those elements forming volatile hydrides—several stages of polyanion formation are detectable. With the

¹⁵ O. Kubaschewski and K. Reinartz, *Z. Elektrochem.*, 1948, **52**, 75.

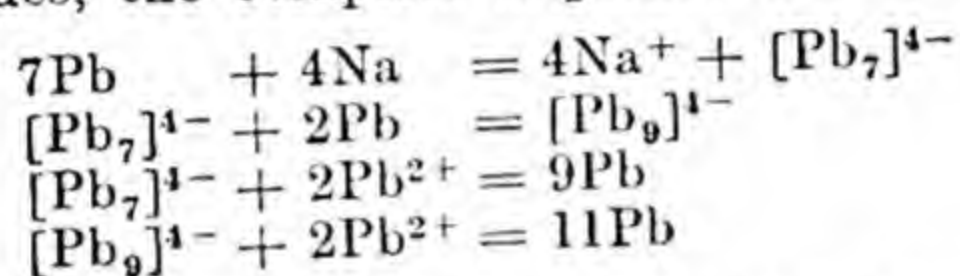
¹⁶ *Naturwiss.*, 1929, **17**, 782; *Z. physikal. Chem.*, A, 1931, **154**, 1, 47; *ibid.*, B, 1932, **16**, 183, 195, 206; *Z. anorg. Chem.*, 1933, **211**, 113.

¹⁷ A. Joannis, *Compt. rend.*, 1892, **114**, 587; *Ann. Chem.*, 1906, [viii], **7**, 75; C. A. Kraus *et al.*, *J. Amer. Chem. Soc.*, 1922, **44**, 1216, 1999, 2722; 1925, **47**, 43; F. H. Smyth, *ibid.*, 1917, **39**, 1299; Bergstrom, *ibid.*, 1926, **48**, 146.

elements of Groups I-III, on the other hand, the same type of reaction with sodium in liquid ammonia forms metallic alloy phases insoluble in liquid ammonia. The compounds formed are summarized in Table 8 (page 472).

Of the compounds listed, those italicized are not soluble in liquid ammonia. They represent, as has already been discussed in an earlier section (p. 446), intermetallic compound phases with completed Brillouin zones, and thus have an essentially homopolar character. The other compounds, however, are soluble, and tend to have intense colours. Thus, Na_3Bi_3 is the colour of permanganate, while Na_4Sn_9 is blood red in solution. In some cases the colour of the solutions by reflected light is complementary to the colour by transmitted light. The liquid ammonia solutions are probably not so much true solutions as sols of aggregated polyanions.

The addition of lead ions (*e.g.* in the form of added lead iodide) to a polyplumbide solution neutralizes the anionic charges until aggregation ensues, the complete sequence of reactions being



In accordance with this typical scheme, the anionic element is deposited at the anode by the electrolysis of solutions of the compounds of lowest sodium content. Thus, lead is deposited anodically from Na_4Pb_9 , but not from Na_4Pb_7 , which is converted at the anode into the higher compound. At the cathode, sodium reacts with the higher compound (Na_4Pb_9), or at a lead electrode cathodic dissolution may occur.

The reaction of metallic sodium with metallic salts is not suited for the isolation of the compounds, since no separation can subsequently be effected from the sodium halides formed simultaneously. The same polyanionic salts, however, are extracted by liquid ammonia from alloys of sodium with the metal concerned. Alloys of sodium and lead, chilled to obtain a fine-grained texture, dissolve readily in liquid ammonia, giving a mixture of both Na_4Pb_7 and Na_4Pb_9 when the atomic ratio Pb : Na in the alloy is less than 9 : 4. Alloys with Pb : Na > 9 : 4 yield pure Na_4Pb_9 , leaving the excess of lead as such, although an alloy of the composition $\text{Na}_4\text{Pb}_{10}$ may be shown by X-ray methods to be a homogeneous metallic phase. Sodium-antimony and sodium-bismuth alloys with 75 atomic per cent of the heavy metal behave similarly.

When the liquid ammonia solutions obtained by the method described in the last paragraph are evaporated, the compounds are

Table 8

Group IV	Group V	Group VI
		Na_2S Na_2S_2 Na_2S_3 Na_2S_4 Na_2S_5 Na_2S_6 Na_2S_7
	Na_3As Na_3As_3 Na_3As_5 Na_3As_7	Na_2Se Na_2Se_2 Na_2Se_3 Na_2Se_4 Na_2Se_5 Na_2Se_6
Na_4Sn_9	Na_3Sb Na_3Sb_3 Na_3Sb_7	Na_2Te Na_2Te_2 Na_2Te_3 Na_2Te_4
Na_4Pb_7 Na_4Pb_9	Na_3Bi Na_3Bi_3 Na_3Bi_5	

obtained as pyrophoric substances of metallic appearance, which are readily and completely soluble in liquid ammonia. The solid substances are, in all cases, ammoniated. They appear to be amorphous in structure, but on deamination the resulting alloy undergoes reorganization, with the formation of an atomic (alloy) lattice.

This behaviour is well illustrated by the polyantimonides and polybismuthides. The lower compounds, $[\text{Na}(\text{NH}_3)_x]_3\text{Sb}_3$ and $[\text{Na}(\text{NH}_3)_x]_3\text{Bi}_3$, on deamination at once form the alloy phases NaSb and NaBi, already known from the fusion equilibria of the binary system. The higher antimonides and bismuthides, $[\text{Na}(\text{NH}_3)_x]_3\text{Sb}_7$, $[\text{Na}(\text{NH}_3)_x]_3\text{Bi}_{5-7}$, form mixed two-phase products of NaSb + Sb, NaBi + Bi, as is shown by X-ray analysis, just as do melts with less than 50 atomic per cent of sodium. That this transformation corresponds to an entire reorganization of the molecules follows from the crystal structures of the alloy phases. NaSb has eight atoms of each kind in the unit cell, NaBi has a body-centred tetragonal atomic lattice. Neither can therefore contain polyatomic anion complexes such as Sb_3^{3-} .

It is plain that the deamination of the sodium ions, by decreasing their size, increases their potential and thereby the deforming action on the anions (in the sense discussed by Fajans, *cf.* Chap. III, p. 42) so far as to break up the anion completely. Only with very large univalent cations is the polarizing action reduced sufficiently for the highly deformable polyanions to be stable. Polyanion formation is thereby limited to the alkali metals, although there is evidence that an unstable polyplumbide of the very large tetramethyl ammonium ion may be formed in solution. The maximum of polyanion formation with the heavy metals is reached with sodium, due probably to the operation of two opposing factors. (a) With increase of size (K, Rb, Cs), the potential of the alkali ions is reduced too far to permit of stable ammination, but, (b), the size of the non-amminated cations is too small, even in the case of caesium, for polyplumbides, etc., to be formed. This behaviour is paralleled, to some extent at least, in the more familiar cases of polyanion formation by sulphur and especially by iodine. Here the same criterion of a minimum cationic size seems to apply, since only the largest alkali metal ions, rubidium and caesium, form anhydrous triiodides. The only stable potassium and sodium compounds have the compositions $KI_3 \cdot H_2O$ and $NaI_3 \cdot 2H_2O$ respectively, and break up if they are dehydrated, as do Zintl's polyanionic salts when they are deaminated. Amongst the higher polyiodides, caesium alone forms an anhydrous salt of the type CsI_4 , while the MI_7 and MI_9 types invariably contain either constitutional water or benzene. The hepta-iodide compound $[Ni(NH_3)_4]I_7$, containing the bulky $[Ni(NH_3)_4]^{2+}$ cation,¹⁸ is noteworthy in this respect.

¹⁸ Ephraim and Mosimann, *Ber.*, 1921, 54, 385; *cf.* also N. S. Grace, *J.C.S.*, 1931, 594; Abegg and Hamburger, *Z. anorg. Chem.*, 1906, 50, 403; Briggs and Geigle, *J. Physical Chem.*, 1930, 34, 2250.

CHAPTER XVI

SOME INTERSTITIAL AND NON-STOICHIOMETRIC COMPOUNDS

The Refractory Carbides, Nitrides and Borides.¹—The carbides, nitrides and borides of the metals of Groups IV, V and VI of the Periodic System constitute a related group of compounds remarkable for their refractory nature and true metallic properties. As will be seen, they are essentially related to the intermetallic compounds, and are included amongst the so-called *interstitial compounds* (see below, p. 476).

All these compounds may be obtained by heating the powdered metal to a high temperature with carbon, boron or in a stream of nitrogen or ammonia, respectively—at 2200° for the carbides, 1800–2000° for the borides, and at 1100–1200° for the nitrides. The compounds are so obtained in the form of powders. They may be purified and compacted by sintering them, in the form of compressed rods, in a vacuum or in an inert atmosphere—*e.g.* in argon—at temperatures between 2500° and their melting-points. All the possible impurities, being more volatile than the refractory compounds, can be thereby volatilized away.

A more convenient process, applicable to all cases, is by carbonization or nitriding from the gas phase. A wire of the metal, for example of tantalum, hafnium or tungsten, for which the method is especially suitable, is heated in an atmosphere of hydrocarbon vapour or nitrogen. In the former case, the partial pressure of the hydrocarbon must be sufficiently low to prevent the deposition of uncombined carbon, in the form of graphite, on the hot wire. The refractory compounds are conveniently obtained in the form of filaments by this process. An alternative method is to use a carrier filament of some other material—platinum, carbon or tungsten—which is heated in the mixed vapours of toluene or methane and a volatile metallic halide; all the metals concerned form volatile halogen compounds. The reaction, proceeding at the surface of the incandescent filament, deposits a coating of the required metallic carbide. In the same way, nitrides may be formed by using nitrogen, and borides by using boron tribromide as con-

¹ For an excellent review, see Becker, *Physikal. Zeitschr.*, 1933, 34, 185.

stituents of the vapour. The metallic carbides, etc., may be obtained by this method in the form of single crystals. The central carrier wire, upon which the deposit was formed, can finally be volatilized away by heating the composite filament almost to its melting-point.

The remarkable physical properties of these compounds are summarized in Table 1. It may be seen that the hardness lies in general between that of diamond (hardness = 10) and topaz (hardness = 8), while the carbides of zirconium, hafnium, niobium (NbC, m.p. 3770°K.) and tantalum are actually less fusible than tungsten, rhenium or even carbon itself. It is, indeed, possible to melt and vaporize carbon in a crucible of sintered tantalum carbide.²

Table 1

Carbides			Nitrides			Borides		
	M.p.	Hardness		M.p.	Hardness		M.p.	Hardness
TiC	3410°K.	8-9	TiN	3220°K.	8-9	TiB		9
ZrC	3805°	8-9	ZrN	3255°	8	ZrB	3265°K.	9
HfC	4160°							
TaC	4150°		TaN	3360°				
W ₂ C	$3130^{\circ*}$	9-10						
WC	3130°	9						
Mo ₂ C	2600°							
MoC	2840°							

(* With decomposition.)

Binary systems of these high-melting compounds present some interesting features. Tantalum carbide and niobium carbide form a complete series of solid solutions melting between 3770°K. and 4150°K. Tantalum carbide and zirconium carbide form a binary system which shows a maximum melting-point of 4215°K. at the composition $4\text{TaC} + \text{ZrC}$ —the highest melting-point recorded for any substance.

All these compounds are extremely inert chemically. Thus, titanium carbide is unaffected by water or hydrogen chloride at 600° , and vanadium carbide is attacked by chlorine or sulphur only at a red heat. All the compounds are more readily attacked by oxidizing agents, such as aqua regia, or by gaseous oxygen at high temperatures. Vanadium carbide is described as being attacked slowly by cold nitric acid. The carbides of molybdenum

² *Ibid.*

and tungsten are somewhat more reactive than the metals themselves. In each case, two carbides, Mo_2C and MoC , W_2C and WC , are well attested; MoC and WC decompose at their melting-points, giving the lower carbide and graphite.

It is plain that the compositions of these substances, like those of the intermetallic compounds, are not determined by the valency of the metal and non-metal components in the ordinary sense. The compounds have much in common with the true metals; thus, they have a high electrical conductivity, with a negative temperature coefficient, showing that true metallic conduction is involved. The order of the conductivities of the compounds of any one metal is usually

free metal $>$ carbide $>$ nitride $>$ boride.

The metallic character extends so far as to include the phenomenon of supraconductivity—the first instance of supraconducting compounds. In some cases, indeed—with niobium carbide at 10.1°K and with zirconium nitride at 9.45°K —supraconductivity sets in at temperatures higher than with any pure metal. Finally, all are weakly paramagnetic, the susceptibility varying but little with temperature. As has been discussed in the previous chapter, the paramagnetism of the conduction electrons is a characteristic property of the metallic lattice.

These properties are reflected in the crystal structure of the compounds. In Chapter V it has been seen that in an ionic lattice, such as the crystal lattice of the silicates, the small metallic cations are interpolated in the cavities of a close-packed structure of large anions. The same holds good for the salt-like carbides dealt with in the next section.

It was originally suggested by Hägg³ that the converse applied to the compounds under consideration, the metal atoms determining the structure with the small atoms of non-metal inserted between them. For this reason, these substances are frequently termed *intermetallic compounds*. Rundle⁴ has shown that this view is an over-simplification, however. All the compounds MX , where X is B , C , N or in some cases O , have the sodium chloride structure, irrespective of whether or not the parent metal M has a close-packed structure. Moreover, even although the formation of the compound may involve a considerable expansion of the metal structure, these compounds are harder and have higher melting-points than the metals. Although the *metal-metal* bonds may be weakened, new *metal-nonmetal* bonds have been formed, and are

³ *Z. phys. Chem.*, 1931, B, 11, 433.

⁴ *J. Amer. Chem. Soc.*, 1947, 69, 1327.

apparently stronger. The hypothesis advanced to interpret these facts links up directly with Pauling's views on metal structures.

Arranged in the NaCl-type structure, every atom has six equivalent neighbours. This would apparently imply the utilization of octohedral bond functions. The atoms of the first short period, however, have only four stable orbitals for bonding. Of these, the p orbitals are mutually at right angles, as is required. Rundle suggests that two bonds may be formed, by resonance, by a single electron pair in each p orbital. If all the orbitals could be used, stronger bonds could be formed. This could be achieved if the orbitals were a pair of $[sp]$ hybrid orbitals and two p orbitals, since resonance would make all the bonds equivalent. The whole really constitutes a metallic system, but with stronger bonds (order $\frac{2}{3}$) than are found in the usual metallic structures.

The refractory carbides find some technical possibilities in virtue of their great hardness. Tungsten and tantalum carbides, in particular, may be alloyed with the metals of the iron group, and alloys of cobalt with tungsten carbide are suited for the manufacture of high-speed tools of very high performance.

The Salt-like Carbides.—The more strongly electropositive metals form carbides which are diametrically opposed in type to the metallic compounds just considered. They are colourless, transparent crystalline solids, non-conductors of electricity, which are decomposed by water or dilute mineral acids with the formation of hydrocarbons. A consideration of the products of hydrolytic decomposition shows that the salt-like carbides may be divided into three groups:

- (a) carbides yielding methane on hydrolysis— Be_2C , Al_4C_3 ;
- (b) carbides yielding acetylene on hydrolysis— Na_2C_2 , K_2C_2 , CaC_2 , SrC_2 , BaC_2 , Cu_2C_2 , Ag_2C_2 ;
- (c) carbides forming mixtures of hydrocarbons, of two types, giving as their products either (i) chiefly acetylene, with some unsaturated hydrocarbons— UC_2 , LaC_2 , NdC_2 , etc.; or (ii) chiefly methane and hydrogen— Fe_3C , Mn_3C , Ni_3C .

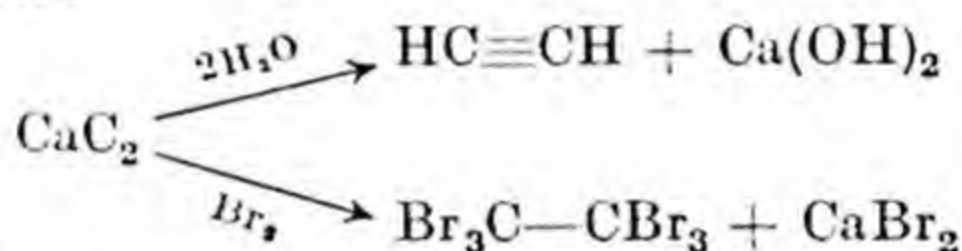
The relation of the hydrolysis reaction to the constitution of the solid carbides has been in large measure elucidated through von Stackelberg's work on their structure.⁵

The salt-like carbides, in contrast to the interstitial carbides, possess ionic lattices, with the metallic cations packed into the interstices between the carbon anions. As such, the salt-like character is dependent upon the sufficiently strong electropositive nature of the metal. Thus, in the simple substitution products

⁵ *Z. physikal. Chem.*, B, 1934, 27, 53.

of methane, Be_2C , Al_4C_3 , SiC , the transition from a true salt to complete homopolar character exactly follows the decline in electropositiveness from beryllium to silicon.

The second factor which determines the nature of the carbides is the size of the metallic cation, in conjunction with its valency. The close-packed structure of anions provides, for each anion, two equivalent 'tetrahedral' cavities for occupation by cations. Hence, if too many cations are needed, there is no room available; from the crystal-chemical standpoint, this is the reason why no 'methane salts' of the alkali metals—*e.g.* Na_4C —exist. The divalent alkaline earth metals could be accommodated as far as their number is concerned, but the size of their cations is such that the anion lattice would be excessively deformed. In consequence, the carbon lattice breaks up into discrete C_2^{2-} anions, the known alkaline earth carbides being the acetylides; the alkali metal cations can be accommodated in similar fashion. The acetylide ion therefore exists as such in the crystal, so that hydrolysis necessarily yields acetylene, and bromination forms C_2Br_6 , the carbon atoms remaining mutually attached:



It is of interest to compare this type of structure and reaction with the corresponding silicide, CaSi_2 . Here the pronounced tendency for silicon to form four homopolar bonds leads to the production of a layer lattice structure, in which calcium ions are situated between sheets of indissolubly linked silicon atoms. The hydrolysis of calcium silicide therefore necessarily leads to the formation of a high molecular unsaturated silene, and the existence of a true silicon acetylene, Si_2H_2 , is excluded *a priori* by the structure of its supposed derivative (*cf.* Chap. XI, p. 344).

A structure related to that of the acetylides must be possessed by a magnesium carbide, Mg_2C_3 , which is described⁶ as forming chiefly allylene, $\text{CH}_3\text{C}\equiv\text{CH}$, on hydrolysis. This would imply that C_3^{2-} units already exist within the crystal lattice.

The carbides of the rare earths, thorium and uranium, of the general formula MC_2 , also contain discrete C_2^{2-} anions. Their hydrolysis follows a somewhat different course from that of the acetylides, however, since the metals are ultimately obtained in the trivalent or quadrivalent states, respectively. Hydrogen is therefore liberated in the reaction with acids, with the result that the

⁶ Novák, *Z. physikal. Chem.*, 1910, **73**, 513: see also Rueggeberg, *J. Amer. Chem. Soc.*, 1943, **65**, 602.

acetylene formed as the initial product is, in part, reduced to ethylene, ethane, methane or other hydrocarbons.

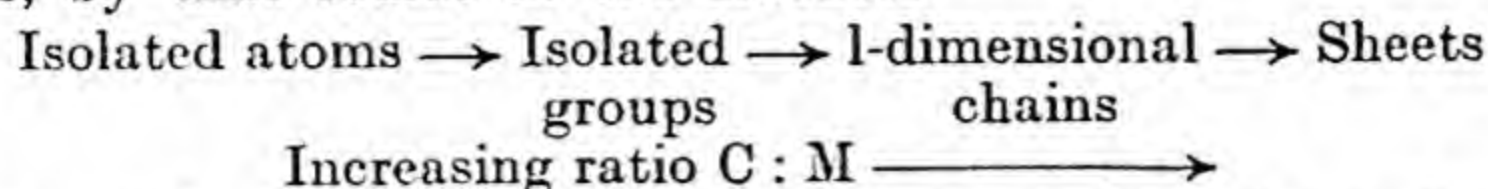
Carbides of the Iron Group.—Iron and its congeners form carbides which are in a sense intermediate between the interstitial and the salt-like types. Structurally, they are related more closely to the interstitial compounds, but they lack the chemical stability and perfect metallic character of the refractory carbides dealt with above. This may be correlated with the smaller radius of the iron group atoms. The formation of interstitial compounds without serious distortion of the metal lattice is possible only when the ratio *radius of metal : radius of carbon* is greater than 1.7—i.e. for metallic atoms with a radius greater than 1.3 Å. Iron (radius 1.26 Å.) is just smaller than this, and the other metals such as manganese (radius 1.18 Å.) are still further removed from the limiting radius ratio. Hence, their carbides, although sharing the metallic characteristics of the interstitial compounds, possess crystal structures distinct from those of the metals, and their properties are modified in other ways.

Cementite, Fe_3C , and the analogously formulated carbides of manganese and nickel, thus possess structures in which the carbon atoms are present as isolated units in the lattice. They are readily decomposed, however, by acids and water. Whereas manganese carbide is decomposed by water to give methane and hydrogen, cementite undergoes a more complex reaction in which methane, ethane, ethylene, hydrogen and even solid and liquid hydrocarbons are formed, while free carbon is deposited. The mechanism of these reactions is unknown. Nickel carbide, Ni_3C , is much less stable than is cementite, while Co_3C , although inferred from thermal analysis of the cobalt-carbon system to exist, cannot be isolated.

The C_2 and C_3 structural units found in the salt-like carbides can be thought of as hydrocarbon chains, stripped of their hydrogen. A stage intermediate between the stripped hydrocarbon anion and the atomic lattice of the interstitial carbides proper is represented by the remarkable chromium carbide, Cr_3C_2 . The crystal structure of this compound shows that the carbon forms long zig-zag chains through a lattice of chromium atoms. The carbon atoms in the chains are about 1.64 Å. apart—i.e. little farther apart than in paraffin hydrocarbons. The whole represents the union of chromium with an infinite paraffin hydrocarbon skeleton, stripped of hydrogen. In a sense, Cr_3C_2 constitutes an aliphatic parallel to the potassium-graphite compounds to be discussed in a later section, since these are, in effect, compounds of the metal with an infinitely extended condensed aromatic network.

The Borides and Silicides.—In the metallic carbides, as has

been seen, compounds may be formed with a progressively increasing ratio of carbon to metal, and manifesting also a progressive increase in structural complexity, of a type paralleled, amongst ionic compounds, by that found in the silicates



It has recently been shown that, amongst the borides and silicides, the varied types of compound found can be classified in a similar way. The ultimate stage, without an analogue amongst the metallic carbides, is found in the borides of the alkaline earths and rare earths—*e.g.* CaB_6 —and in silicides such as ThSi_2 , in which the non-metal atoms build up a three-dimensional network with metal atoms in interstitial positions. In these, and in the hexagonal, pseudo-graphitic sheets of boron or silicon atoms in CrB_2 , $\beta\text{-USi}_2$, etc., there is a continuous fabric of strong bonds throughout the structure. The great hardness and high melting-points frequently found amongst these compounds reflect their adamantine character. Silicon shows a marked tendency to form sheet and network structures in the silicides, and in the hydrolysis of the alkaline earth silicides the extended two-dimensional fabric of silicon atoms may persist; the compounds formed by such processes are the siloxenes, discussed in a previous chapter. The compounds KSi_8 , RbSi_8 , formed by the direct union of the alkali metals with silicon, are of interest when compared with the compounds formed by the alkali metals with graphite (*see below*). As the only known form of silicon has the diamond structure, it is to be supposed that in these alkali silicides the three-dimensional network of silicon atoms persists, with metal atoms in the interstices.

The regular progression of structural type with changes in the metal : non-metal ratio is summarized in Table 2.

Table 2

<i>Single Atoms</i>	<i>Pairs of Atoms</i>	<i>Chains</i>	<i>Hexagonal Sheets</i>	<i>3-dimensional Networks</i>
Mo_2B W_2B		CrB MoB WB	CrB_2 Mo_2B_5 W_2B_5	
U_3Si FeSi	U_3Si_2	USi FeSi_2	$\beta\text{-USi}_2$	CaB_6 , LaB_6 $\alpha\text{-USi}_2$
Fe_3C	CaC_2 , LaC_2	Cr_3C_2	KC_{16} , KC_8	KSi_8

Graphitic Compounds. [i] **Graphite.**—The most perfect development of the layer lattice type of structure is found in graphite. This consists of sheets of carbon atoms, linked in hexagonal array as in condensed aromatic skeletons, such as pyrene, so that each sheet constitutes a giant aromatic molecule (Fig. 62). The spacing of the carbon atoms within each sheet, 1.4 Å., is about the same as that between the carbon atoms of aromatic ring systems. Such sheets of carbon atoms are superimposed, one upon another, at a spacing of about 3.4 Å.; the exact interplanar distance is slightly variable, and opens up appreciably when the area of the sheets becomes very small—*i.e.* for very small crystallites. Rather more than three valencies of each carbon atom are utilized (statistically) in carbon-carbon linkages within each sheet. The residual bonding takes the form of a sort of

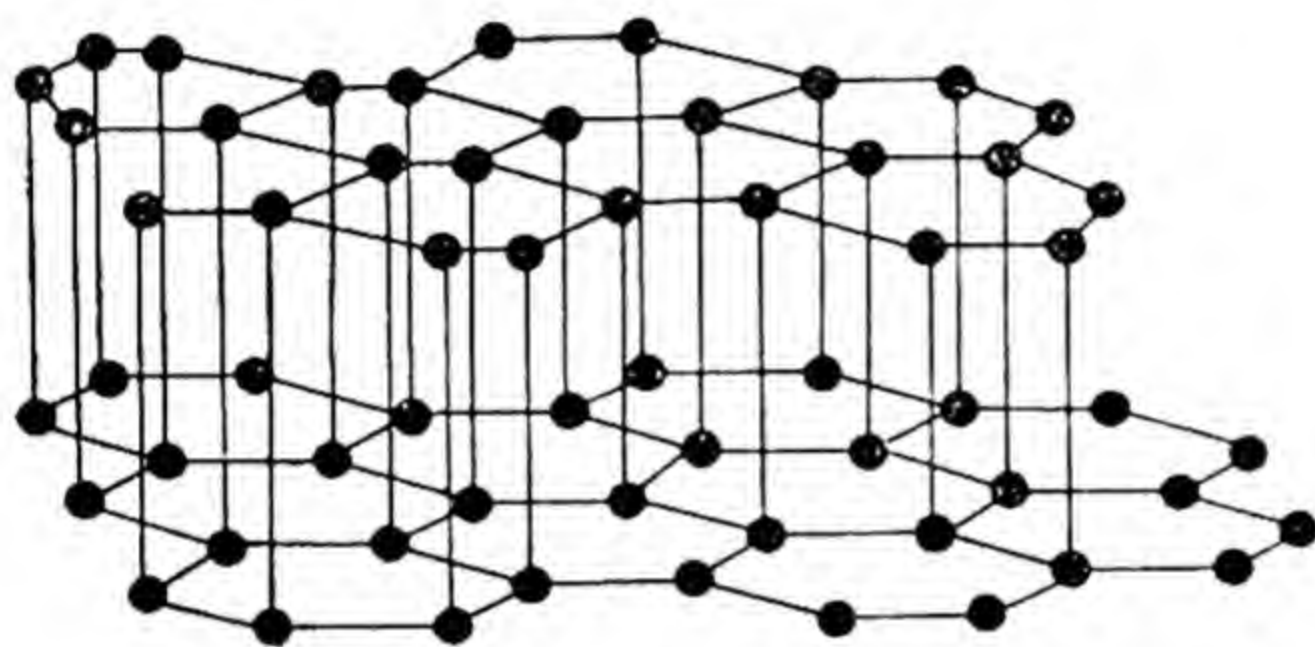


FIG. 62.—Structure of graphite.

metallic linkage between the superposed sheets, which—as their considerable distance apart shows—are but loosely bound together.

The characteristic properties of graphite are, therefore, the possession of metallic electrical conduction and, above all, the ready cleavage across the feeble interplanar forces, whereby the sheets may slip bodily over one another. It is this second consequence of the graphite structure which confers on graphite its lubricating properties. The peculiarities of the structure are also reflected in the chemical properties of graphite, and lead to the formation of compounds in which atoms or radicals are introduced between the graphite sheets.

All forms of carbon, other than diamond, have been found to be graphitic in character. The variation in properties and apparently amorphous character of charcoals arise from the varying size of the unit crystallites and the differing extents to which they are ordered regularly within the particle. In the finest lamp black, or in norite, the crystallites are said to be only of the order of 40–50 Å.

across, and 10 Å. thick—*i.e.* each contains only two or three layers of carbon sheets, a few hundred rings in extent. In the reddish form of carbon deposited from carbon suboxide the size of the particles is even smaller than this (*cf.* p. 321).

[ii] **Graphite-Potassium Alloys.**—It was first observed by Fredenhagen⁷ that graphite is wetted, and immediately penetrated by liquid potassium, at the same time swelling up and disintegrating. If any excess of potassium be evaporated off in vacuum, a pyrophoric coppery-red mass remains; on stronger heating a blue-black substance is formed and finally the original amorphous charcoal or graphite is regenerated. It is significant that, with crystalline graphite, the crystal form is retained throughout; swelling takes place only in the direction perpendicular to the laminations. Both with finely divided charcoal and with graphite, two distinct stages may be distinguished—a bronze-coloured potassium-rich stage and a steel-blue product obtained by partial removal of potassium. These two stages were shown by Fredenhagen to correspond to definite dissociation pressures of potassium, and thus to represent two distinct compounds, C_8K and $C_{16}K$, respectively. The potassium may be washed out of these by means of mercury, showing that the metal is loosely held; graphite is thereby regenerated.

The X-ray examination of the compounds discloses that the graphite sheets are unaltered by the reaction with potassium.⁸ Swelling takes place, as stated, along one dimension only, and corresponds to an increase in the interplanar spacing; it arises from the entry of potassium atoms between the sheets. The potassium-rich stage, C_8K , has one potassium atom for each eight carbon atoms inserted between every pair of graphite sheets. In the second stage, $C_{16}K$, potassium atoms are similarly ordered, but are inserted only between alternate graphite layers.

[iii] **Graphitic Oxide.**—It has been known for many years that when graphite is treated with strong oxidizing agents—*e.g.* with potassium chlorate and nitric acid, or with potassium chlorate, nitric and sulphuric acids—both oxygen and hydrogen are taken up. The eventual product is a substance of variable colour, ranging from green to brown, which retains the outward crystal form of the original graphite, although undergoing considerable swelling. Early workers, in view of the ease with which the product can be dissolved or peptized by alkalis, considered that one or more *graphitic acids* were formed.⁹ Brodie assigned to graphitic acid

⁷ *Z. anorg. Chem.*, 1926, 158, 249; *ibid.*, 1929, 178, 353.

⁸ Schleede and Wellmann, *Z. physikal. Chem.*, B, 1932, 18, 1.

⁹ See, for example, Mellor, *Comprehensive Treatise*, Vol. V, p. 828.

the formula $C_{11}H_4O_5$, but other workers held that various stages of oxidation could be distinguished, corresponding with the various colours of the product.

The so-called graphitic acid may be reduced by stannous chloride, hydrogen sulphide or hydroxylamine to a substance which was formerly described as closely resembling graphite in its physical properties, but still containing hydrogen and oxygen. Graphitic acid itself decomposes almost explosively when it is heated. Oxygen is not set free, but carbon monoxide and dioxide are formed, and a residue is left which consists either of amorphous carbon or of a carbonaceous substance much poorer in oxygen than is graphitic acid, which Brodie called pyrographitic acid. This solid residue is readily attacked by oxidizing agents, forming ultimately mellitic acid, $C_6(CO_2H)_6$, amongst other products. It can now be seen that this residue must consist of graphite, possibly retaining a little oxygen, which is reactive towards oxidizing agents in virtue of the small size and disintegrated character of its crystallites.

The true nature of graphitic acid, and of its chemical reactions, has been in large measure cleared up by the work of U. Hofmann and his school.¹⁰ They have shown that graphitic acid, like the potassium-graphite alloy, is a compound in which the graphite sheets enter into chemical combination without any severance of the bonds making up their carbon skeletons. The weak forces between the sheets are destroyed, and oxygen is attached to the carbon atoms by that fourth valency not involved in carbon-carbon bonds. As a result, the metallic character, lustre, and hydrophobic character of graphite are lost. Graphitic acid is hygroscopic, and is less wetted by non-aqueous solvents than is graphite; in place of a metallic lustre, it has a colour varying from green to brown according to the composition.

The older conception of Brodie's graphitic acid was early disproved, although Thiele¹¹ assigned to it the ideal formula $C_6(OH)_3$. It has been shown that most of the hydrogen contained in graphitic acid is present in the form of water, a conclusion already drawn by Hulett and Nelson from the mode of dehydration of graphitic acid. They suggested that it had the true composition, $C_{2.7-3}O$, with water adsorbed on the relatively large surface of the colloidal material. The water content may vary up to 35 per cent, and its variation is accompanied not only by the colour changes which misled early investigators into a belief in the existence of several different compounds, but also by the phenomenon of uni-dimensional

¹⁰ *Ber.*, 1928, 61, 435; 1930, 63, 1248; *Z. Elektrochem.*, 1931, 37, 613; *Kolloid Zeitschr.*, 1932, 58, 8; 61, 297; *Annalen*, 1934, 510, 1.

¹¹ *Kolloid Z.*, 1931, 56, 129; 1948, 104, 114.

swelling already referred to. The distances between the carbon atoms in the graphite sheets are unaltered, since the sheets remain intact, but the insertion of oxygen atoms between the sheets forces them apart, altering the spacing from 3.4 Å. to a value between 6 and 11 Å.; this interplanar spacing increases regularly with the amount of water in the material.

In alkaline media, the swelling proceeds even further, and probably corresponds to the complete resolution of the skeleton into individual sheets of atoms. The viscosity of the suspensions is high, and the graphite passes into colloidal solution. It is plain that each graphite oxide sheet constitutes a macro-molecule, the oxide sheets being held together by the intermolecular van der Waals forces only. The swelling process reaches completion when there is room for two layers of water molecules between the sheets, *i.e.* when each sheet is covered on both sides with a unimolecular film of water.

The material has cation-exchanging properties after peptization by alkali, and the 'acid' form can neutralize up to 5–8 milliequivalents of alkali per gram of graphitic acid. This amount is too great to be accounted for only by —COOH groups or acidic —OH groups formed by carbon atoms on the edges of the graphitic sheets. It implies that reactive hydroxyl groups are located also at points on the sheet, remote from the edges. Ruess¹² has been able to methylate carefully dehydrated graphitic oxide by means of diazomethane, and the methoxyl content of the product agreed roughly with the capacity of the graphitic acid for neutralizing alkali. The effect of methylation was to increase yet further the spacing between the graphitic sheets, from 6.3 Å. to 8.5 Å.—evidence for the presence of bulky methoxyl groups between the sheets. Graphitic oxide has been acetylated in a similar manner.

From the work of Hofmann and Ruess, it would appear that graphitic acid can be regarded as substantially a *graphitic oxide*, in which the ratio C : O may vary, probably up to the limiting formula C_2O . The oxygen atoms appear to be attached, each to two carbon atoms as in ethylene oxide, at a distance of 1.4 Å. above or below the carbon sheets (Fig. 63). The reactions of neutralization, methylation and acetylation require that about one —OH group reacts for every 6–8 carbon atoms. It is, however, not certain whether oxygen is necessarily present in two forms—as ethylene oxide type groups and as hydroxyl oxygen—or whether a proportion of the ethylene oxide groups is reactive, and readily opened by hydration. It is of interest that the compound is essentially non-stoichiometric in composition. During its forma-

¹² *Kolloid Z.*, 1945, **110**, 17.

tion or reduction the composition varies continuously, the graphitic oxide behaving as a homogeneous solid throughout.

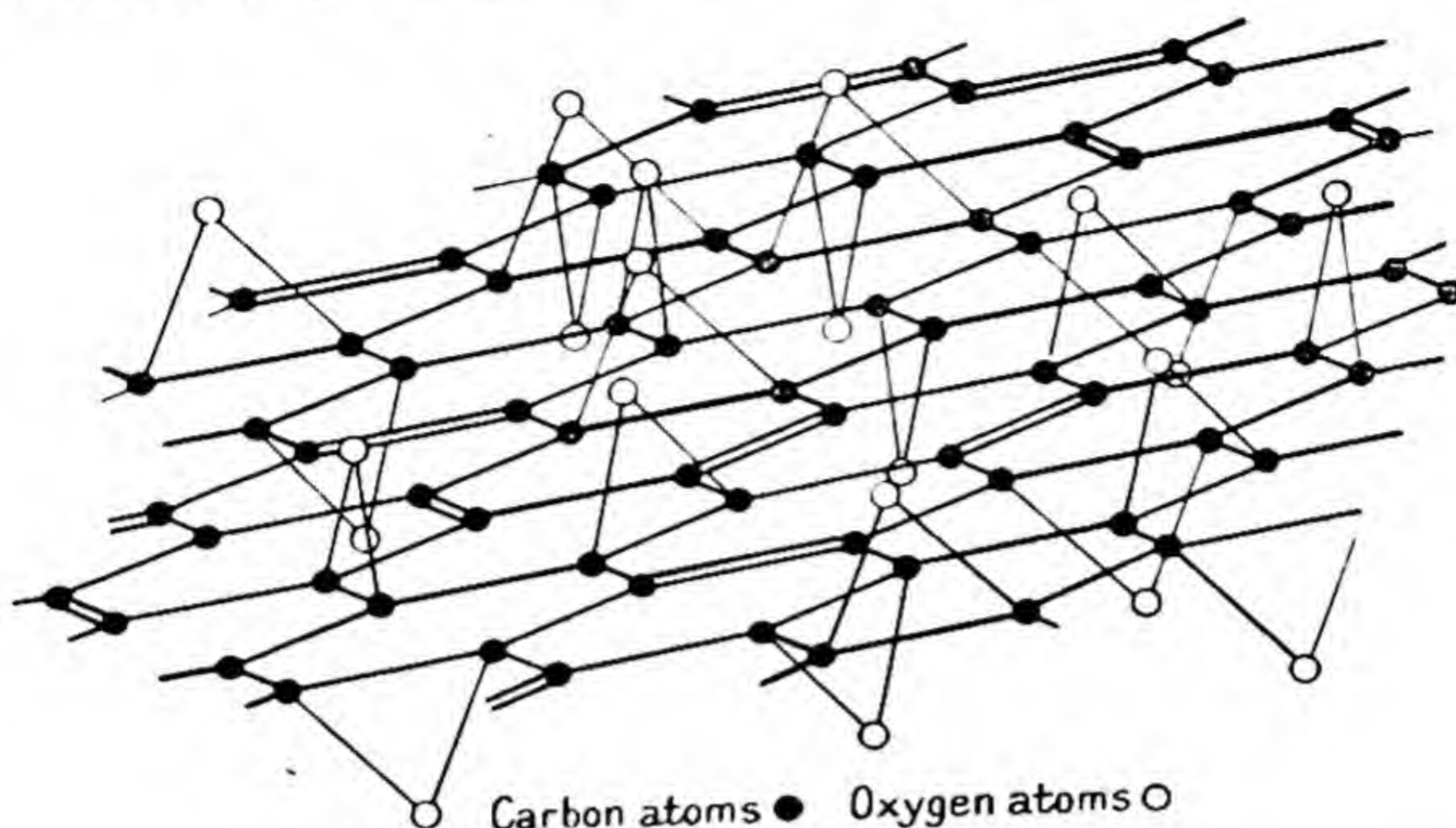


FIG. 63.—The structure of graphitic oxide.

[iv] **Graphite Salts.**—A contrast in certain respects to the graphitic oxide just considered is provided by another class of compounds, the salts of graphite with oxyacids. One of these compounds has long been known, though imperfectly understood until the whole field was clarified by the work of Hofmann and Rüdorff. Graphite suspended in sulphuric acid swells or intumesces in the presence of small amounts of strong oxidizing agents, becoming at the same time purple or blue in colour. This 'blue graphite' cannot readily be isolated, since it reverts to ordinary graphite if the attempt be made to wash it free from sulphuric acid by means of water, but it has been long known that the partially reconverted products contain some tenaciously held sulphuric acid. The formation of 'blue graphite' and its subsequent decomposition by heat has been used for the technical purification of graphite; as will be seen, such treatment modifies chemically the hydrophobic nature of the material.

If the adhering sulphuric acid be washed out of 'blue graphite' by means of phosphoric acid, the product still contains up to about 0.32 gram of sulphuric acid per gram of graphite.

The properties of this substance can be explained in terms of the formation of a graphite bisulphate,¹³ essentially salt-like in nature. In a sense this is a salt derived from one stage in the formation of

¹³ *Z. Elektrochem.*, 1934, 40, 511.

graphitic oxide, and its formation involves the oxidation of the graphite.

Its reconversion to graphite by the action of water is a reduction ; oxygen is not set free, however, as such, but remains bound in part as a surface oxide, so that the regenerated graphite invariably retains 1–2 per cent of oxygen. Some direct oxidation to graphitic oxide takes place during the formation of blue graphite. Both modes of attachment of oxygen to the resulting graphite introduce hydrophilic groups. The treatment of graphite with sulphuric acid under oxidizing conditions is therefore particularly suited to the production of colloidal graphite.

From the consumption of oxidizing agent in its formation, and from the structure worked out from X-ray data, it appears to contain about one HSO_4^- ion per 24 carbon atoms. The total amount of sulphuric acid that can be washed out of the compound corresponds, however, to one SO_4^{2-} ion per 8 carbon atoms, approximately. It has, accordingly, been assigned the composition $[\text{C}_{24}]^+.\text{HSO}_4^-.2\text{H}_2\text{SO}_4$.

It is, indeed, a representative of a class of *graphite salts*, $[\text{C}_{24}]^+.\text{X}^-.2\text{HX}$, where X may be HSO_4^- , ClO_4^- , NO_3^- , H_2PO_4^- or $\frac{1}{2}\text{H}_2\text{P}_2\text{O}_7^{2-}$. They may be formed by the same general method as the bisulphate.¹⁴ An analogous fluoride, $[\text{C}_{24}]^+.\text{HF}_2^-.4\text{HF}$,¹⁵ has also been obtained by the anodic oxidation of graphite in the presence of anhydrous hydrogen fluoride. In principle, the formation of these salts, in which the graphite sheets constitute giant cations, is strictly comparable with the formation of the triphenylmethyl carbonium ion, $(\text{C}_6\text{H}_5)_3\text{C}^+$, from the much smaller resonant aromatic system of the triphenylmethyl radicle, in the same way that the graphite potassium alloy is the analogue of the triphenylmethyl alkali compounds. It is a characteristic of extended aromatic resonance systems that they may function either as donors or as acceptors of electrons.

The acid content of the graphite salts can be decreased in stages by treating the blue graphite with reducing agents or, very strikingly, with a suspension of graphite which is thereby itself converted to a graphite salt. The degree of swelling is diminished at the same time, and runs exactly parallel to the amount of bound acid.

Hofmann and Frenzel showed for graphite bisulphate that, in the stage richest in sulphuric acid, the HSO_4^- ions and H_2SO_4 molecules are introduced between every pair of graphite sheets, thereby increasing the spacing from 3.4 Å. to 7.98 Å. (Fig. 64). In

¹⁴ W. Rüdorff and U. Hofmann, *Z. anorg. Chem.*, 1938, 238, 1.

¹⁵ W. Rüdorff, *ibid.*, 1947, 254, 319.

the graphite salts, unlike graphitic oxide, the variation in composition during progressive reduction is not accompanied by a statistical state of homogeneity; the degradation proceeds in discrete stages. Sulphuric acid is removed in such a way as to leave

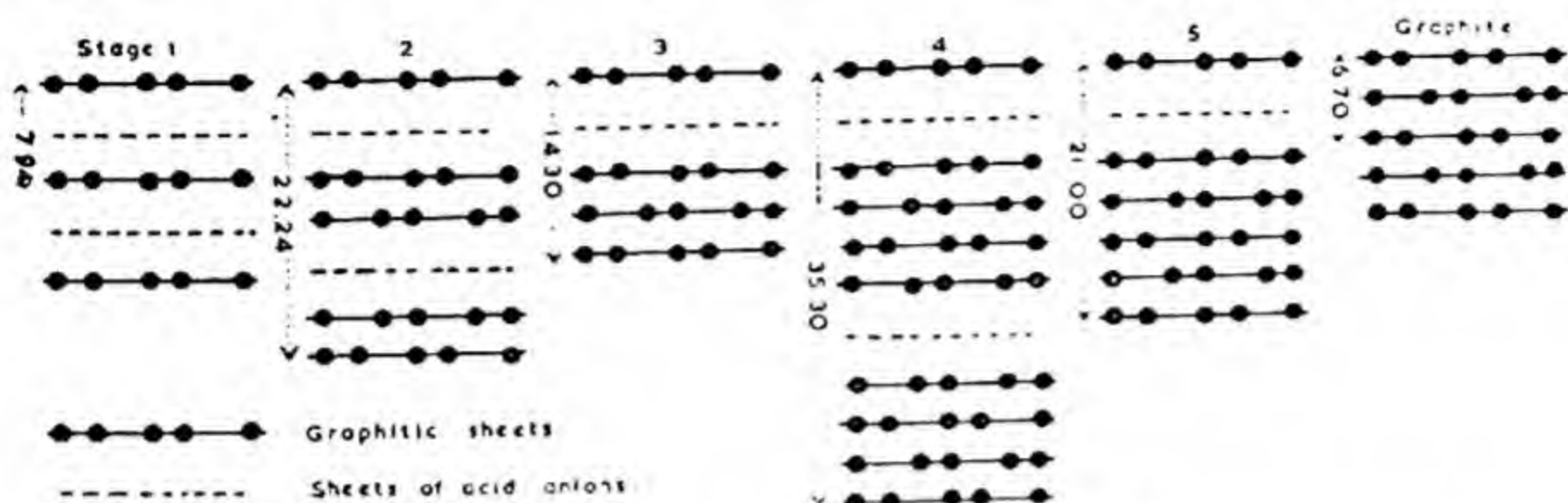


Fig. 64.—Successive stages of reduction of graphite perchlorate: reduction of graphite bisulphate proceeds in similar stages.

graphite spacings and widened spacings arranged in regular array, thereby giving rise to several distinct stages in the swelling process. In the first stage, every pair of graphite sheets has acid groups interposed; at the second stage, every other pair, and so through the reduction cycle. The *c* axis of the crystal, measuring the length of the 'repeat' in the structural pattern, thus progressively increases, and the process can be followed through at least five stages.

Stage 1	$c = 15.96 \text{ \AA.} = 2 \times 7.98$	HSO_4^- between every pair of planes
2	$22.66 = 2 \times (7.98 + 3.35)$	between every 2nd pair of planes
3	$29.44 = 2 \times (7.98 + 2 \times 3.35)$	between every 3rd pair of planes
5	$42.92 = 2 \times (7.98 + 4 \times 3.35)$	between every 5th pair of planes

The behaviour of the other graphite salts is exactly similar.

[v] **Carbon Monofluoride.**—In recent investigations on the chemistry of fluorine, the electrolytic method of preparation first used by Moissan has been modified by the substitution of carbon electrodes for the costly platinum-iridium used by him (see Chap. XI, p. 352). It has frequently been observed that the anodic liberation of fluorine is attended by a considerable swelling of the carbon electrodes, and by a large increase in the resistance of the cells. Such effects are occasionally accompanied by the occurrence of violent explosions.

Investigating the origin of these phenomena, Ruff and Bretschneider¹⁶ found that at fairly low temperatures, and especially at low pressures, both graphite and amorphous carbon (*i.e.* finely crystalline, disordered graphite) absorb fluorine without igniting. A grey hydrophobic product, having the limiting composition CF , is obtained from graphite at temperatures below 500° , or from norite, the least crystalline form of carbon, at $280\text{--}450^\circ$. This carbon monofluoride varies somewhat in properties according to the kind of carbon used for its preparation. According to Rüdorff,¹⁷ this is because the reaction comes nearly to a standstill before the ideal composition is reached. Material brought to the composition $\text{CF}_{0.988}$ was silver-white in appearance, and transparent, having lost all the quasi-metallic properties associated with graphite. It had a specific resistance 10^5 times that of graphite, and its formation and subsequent decomposition account for the phenomena observed in the preparation of fluorine. The compound decomposes explosively when it is heated, that obtained from graphite yielding the volatile fluorides CF_4 and C_2F_6 , in addition to free carbon. The carbon monofluoride obtained from norite yields decomposition products with a lower mean ratio of C : F than that from graphite, and amongst the volatile fluorides identified by Ruff and Bretschneider was the unsaturated C_2F_4 . Carbon monofluoride does not react with hydrogen at 400° , proving that the fluorine is combined chemically, and not adsorbed; it may be reduced, however, to the original form of carbon by means of zinc dust and acetic acid.

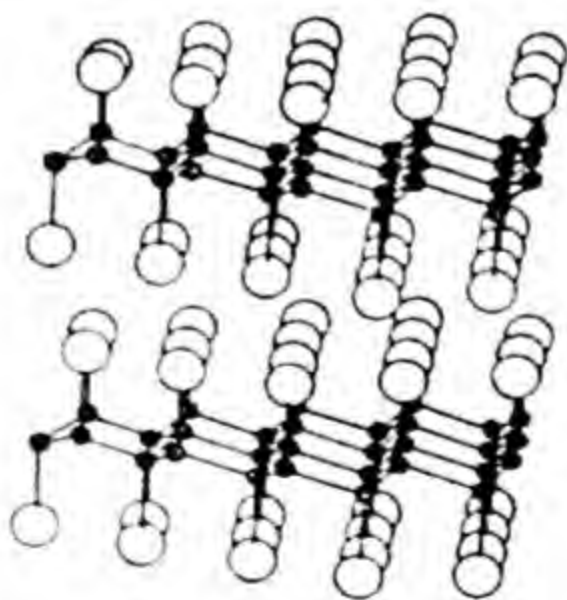


FIG. 65.—The structure of carbon monofluoride.

The low reactivity of the fluorine, the physical properties of the compound and its chemical inertness as compared with the graphite salts all point to a quite different constitution. The composition CF would permit of every carbon atom being covalently bound to fluorine, and to its three carbon neighbours. All vestige of aromatic

¹⁶ *Z. anorg. Chem.*, 1934, 217, 1.

¹⁷ *Ibid.*, 1947, 253, 281.

character would thereby be lost; the carbon atom would then form tetrahedral bonds and the originally planar graphite sheet would give place to puckered sheets of carbon atoms, with fluorine atoms alternatively above and below the sheets (Fig. 65). This constitution is in general accord with the increase in volume produced by the formation of carbon monofluoride, and the increase in length of the basal plane spacings and the c axis spacing as fluorination proceeds. This constitution has, however, not been unequivocally confirmed by the X-ray evidence.

[vi] Molecular Compounds of Graphite with Bromine and Ferric Chloride.—As well as reacting anionically towards the alkali metals, and cationically towards acids, graphite combines in a highly selective manner with certain molecules. Thus it swells in contact with bromine at the ordinary temperature, taking up approximately one Br_2 molecule per 16 carbon atoms, whilst the c spacing increases from 3.4 to 7.05 Å. There can be no doubt, from this evidence, that bromine enters between the planes of the graphite structure. However, the graphite-bromine complex is formed only in saturated bromine vapour, and the bromine is readily lost again by evaporation in a stream of inert gas. It would thus appear that there is little evidence for the formation of a salt-like graphite bromide; it is to be presumed that bromine enters the graphite structure in the form of undissociated Br_2 molecules.

Ferric chloride is also absorbed by graphite, at 180°C ., and three distinct stages of compound formation can be observed, corresponding closely to the step by step degradation of the graphite salts. The stage richest in ferric chloride, with FeCl_3 molecules introduced between every pair of graphite sheets, is stable up to 300° . A portion of the ferric chloride can be removed by washing; that combined within the graphite is not only resistant to leaching, but is neither hydrolysed nor hydrated by treatment with aqueous solutions, and is resistant towards reduction.

As with other graphite compounds, the formation of the complex produces swelling and increase in the c spacing of the graphite. The spacing between sheets of carbon atoms is increased to 9.4 Å., allowing space for the incorporation of FeCl_3 molecules. The dimensions of the graphite structure and of the FeCl_3 molecule suggest that the largest concentration of ferric chloride that could be accommodated by close alignment of the molecules would be one FeCl_3 for 6 C atoms, a composition not out of accord with the observed composition of stage 1, *i.e.* 1 FeCl_3 per 5.9–9 C atoms. Exhaustive leaching leaves a residue with the composition $\text{C}_{12}\text{FeCl}_3$, in which the ferric chloride is very firmly bound: it may be lost by volatilization, to form stage 3 at 300° and graphite above 410° ,

but its latent heat of sublimation (61 k.cal. per mol.) is nearly twice that of free ferric chloride (32 k.cal. per mol.).

It has been suggested that this compound can be compared with the addition compounds formed by ferric chloride with aromatic hydrocarbons, and attributed to the polarization of the π -electrons of the structure. However, the formation of the graphite complex is remarkably specific, since CrCl_3 and even AlCl_3 , which readily forms aromatic addition compounds, show no evidence for swelling and absorption with graphite.

Non-Stoichiometric Compounds.—We have seen in this and the preceding chapter that variability of composition is not infrequently encountered amongst the intermediate phases of metallic systems, and amongst the quasi-metallic adamantine and graphitic compounds. We are, accordingly, accustomed to accept as compounds those phases which have structures distinct from those of their components, even though in a few cases the idealized formula lies outside the range of stable existence of the phase. It is less familiar that this behaviour is not peculiar to the metallic state, but is observed also amongst compounds of essentially ionic type, such as the metallic oxides. Any crystalline compound built up from discrete molecules, identical in the solid and in the vapour (or solutions), necessarily has an invariable composition. Amongst the generality of inorganic compounds, however, based as they are upon co-ordination structures, compounds of fixed composition are probably to be looked upon as a limiting case, and not fundamentally distinct from the grossly non-stoichiometric compounds.

This outlook accords with the quite general conclusions reached by applying statistical thermodynamics to the equilibrium in a crystal lattice.¹⁸ In a compound AB_n , the concept that every atom is on an appropriate lattice point, and every lattice point tenanted by the right kind of atom, is an idealization of the real crystal—representing the equilibrium state at the absolute zero of temperature. In the real crystal, at temperatures above absolute zero, the thermal vibration of the atoms makes possible the occurrence of lattice defects; it is necessary to take into account the interchange of A atoms and B atoms between their proper lattice positions, the location of atoms of A or B in interstitial positions, or the existence of vacant sites, from which A atoms or B atoms are missing. In ionic compounds, any interchange of A for B is highly improbable for energetic reasons, although as has been seen, it is important in metallic phases. The other two types of defect may, however, be present, and are in fact involved in those phenomena—*e.g.* ionic conductivity and chemical reactions—which are associated with

¹⁸ W. Schottky and C. Wagner, *Z. phys. Chem.*, 1930, B, 11, 163.

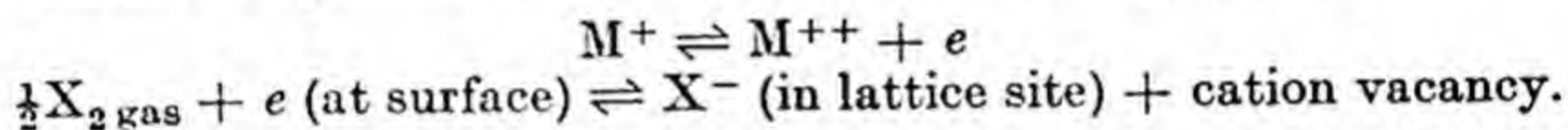
diffusion processes in solids. Thus, in silver bromide, there is reason to suppose that the face-centred cubic lattice of bromide ions is substantially perfect, but that an appreciable proportion of silver ions, approaching 1 per cent at the melting-point, is in interstitial positions, a corresponding proportion of silver lattice sites being vacant. In other cases (*e.g.* lead sulphide), there may be a negligible concentration of interstitial atoms, but vacancies may be present in the lattice positions properly occupied by both metal and non-metal atoms.

As long as a crystalline phase has the ideal stoichiometric composition, there must be a balance between the numbers of defects of each type. Thus in solids like silver bromide, with so-called Frenkel defects, the number of vacant cation sites must equal the number of interstitial cations. For the other limiting case ('Schottky defects'), the numbers of vacant cation sites and vacant anion sites must be equal. Any unbalance between the concentrations of the two types of defect present creates an excess of one or other component. In this way, a polar compound of the ideal formula AB could incorporate an excess of the non-metal B either (*a*) through the presence of a greater concentration of interstitial B atoms than of vacant B sites (an interstitial solid solution type phase), (*b*) by having a higher concentration of vacant A sites than of interstitial A atoms, and (*c*) by having more vacant A sites than vacant B sites. The last two could be described as having a deficiency of A rather than an excess of B ; they are sometimes termed subtractive solid solutions.

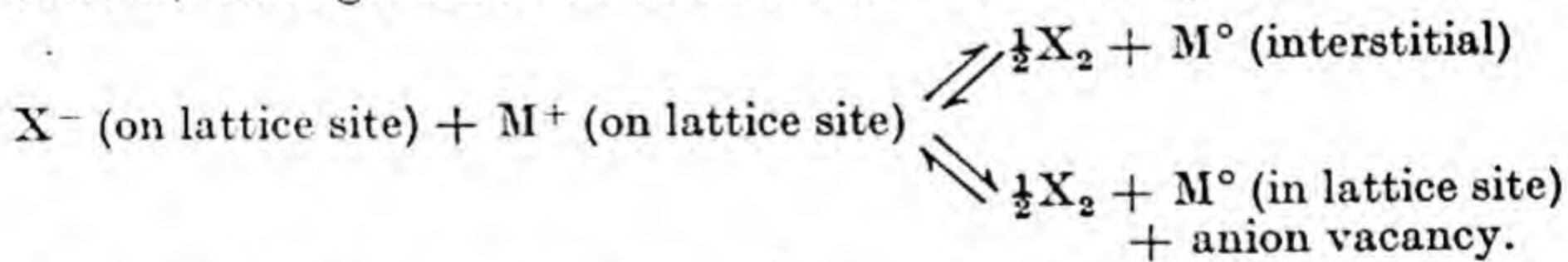
The potential energy of an ion in an interstitial position is higher than that of an ion on a lattice site; a vacant site can be regarded as produced by transporting an atom from the interior of the crystal lattice to a position on the surface. The creation of a lattice defect of either type is thus an endothermic process. However, if a crystal contains a certain concentration of vacant sites or interstitial atoms, the distribution of these over all the lattice sites or interstitial positions of the crystal can be accomplished in a large number of different ways. The defects introduce a certain randomness into the crystal, and so raise the configurational entropy S . Calculation shows, in fact, that although formation of defects raises the total energy H , the free energy $G (= H - TS)$ of an ideal crystal lattice at $T > 0^\circ \text{K}$ would actually be greater than that of a crystal lattice containing a certain finite concentration of lattice defects. The equilibrium concentration, corresponding to the state of minimum free energy, may be shown to increase exponentially with rise of temperature, and since the energy expended in producing defects enters into the exponential factor, it is comprehensible that

the concentration of lattice defects may vary widely from one compound to another. In purely ionic compounds of fairly high or very high melting-point, such as calcium oxide or potassium chloride, the equilibrium concentration is infinitesimally small at the ordinary temperature. Even in these cases, however, it is probable that the concentration may reach significant values at temperatures approaching the melting-point.

The foregoing considerations apply to a compound of ideal composition. In an ionic compound, at least, deviations from stoichiometric composition are contingent on the possibility of a valency change on the part of one or other component. If this is energetically permissible, an unbalance between two sorts of lattice defects can be created by a reaction between the crystal and its environment. Thus, if a compound MX is in contact with the vapour of the non-metal X_2 (*e.g.* cuprous iodide in iodine vapour), there is a mechanism for creating vacant cation sites without changing the concentrations of interstitial cations or vacant anion sites, provided that the ion M can increase its valency. Thus, at the surface, equilibrium is established in the processes



A stoichiometric excess of the non-metal X is thereby built into the crystal, and a corresponding number of cations undergoes an increase in valency. Alternatively, a stoichiometric excess of metal can be brought about by lowering the valence state of a proportion of the cations, through removal of X atoms from the system:



The valence change involves a change in the total energy of the system; the lattice defects simultaneously created will raise the entropy. As before, the equilibrium conditions can be worked out, and it emerges that the concentration of lattice defects of each kind depends on the partial pressure of X_2 (or of M) with which the crystal is brought into equilibrium, as well as on the temperature. The equilibria indicated above are shifted by a change in the vapour pressure of X_2 , and at any temperature the ideally stoichiometric compound MX can exist only under specified conditions.

As a deduction from thermodynamic reasoning, this conclusion should be of general validity. In practice, observable departures from stoichiometric composition are found only in compounds

fulfilling certain conditions. In the first place a valence change is involved. A decrease in valency is possible for any cation—even for the inert-gas type cations, such as K^+ or Ca^{2+} . It may be expected that even compounds of the most electropositive metals—*e.g.* CaO —might form metal-excess phases; this may perhaps be true for oxides such as lime at very high temperatures, but there is only scanty evidence on this point. In order that an excess of non-metal may be incorporated, it is necessary for some of the cations to undergo an increase in valency, and for energetic reasons it may be expected that this type of deviation from ideal composition will be encountered chiefly amongst compounds of the transition metals. It is necessary, moreover, that the formation of lattice defects in the ideal compound should be not too endothermic a process, and that the sizes of the ions in the two valence states should be not too different, so that the crystal lattice is not distorted to the point of collapse. The nett effect of these restricting factors is that non-stoichiometric polar compounds are most common amongst the compounds of the transition metals with highly polarizable non-metals (*e.g.* sulphur). There are, however, some striking examples amongst the oxides of the transition metals, and a few systems are briefly discussed below.

The nature of the lattice defects giving rise to the non-stoichiometric character can frequently be ascertained by comparing the observed density of the solid compound with that calculated from X-ray measurements of the unit cell dimensions. Thus ferrous sulphide, nominally FeS , actually exists over the composition range $FeS_{1.00}$ to $FeS_{1.14}$. If this were due to the incorporation of extra, interstitial sulphur atoms, the mean weight per unit cell would increase with the sulphur content. The cell dimensions of phases of variable composition usually alter with the composition, but when allowance has been made for this, the density of pyrrhotite should increase markedly with its sulphur content. If, alternatively, the phase is actually deficient in iron, so that the unit cell could be assigned the average formula $Fe_{1.00}S$ to $Fe_{0.88}S$, there should be a progressive diminution in density as the sulphur content increases. The observations of Hägg and Sucksdorf¹⁹ leave no doubt that the latter interpretation is correct.

The ferrous sulphide system is typical of the sulphides, selenides and tellurides of the transition series.²⁰ These are not purely ionic compounds; they possess the $NiAs$ type MX structure, or cadmium iodide or pyrite type MX_2 structures associated with large polarization effects, and frequently have metallic conductivity and abnormal

¹⁹ *Z. phys. Chem.*, 1933, B, 22, 444; *Nature*, 1933, 131, 167.

²⁰ See summary and review in *Chem. Soc. Ann. Rep.*, 1946, 43, 104.

magnetic properties. As has been stated, however, the same metals form non-stoichiometric oxides also. Thus it is remarkable that stoichiometric ferrous oxide is non-existent. It was first observed by Schenck and Dingmann²¹ that the compound regarded as ferrous oxide (known as wüstite), which exists in stable equilibrium with iron or magnetite only at temperatures above 580°, invariably contains at least 5 atoms per cent of oxygen more than would correspond to the formula FeO. A recent careful study of the phase equilibria in this important system²² confirms that wüstite exists over a composition range extending at 1400° C. from FeO_{1.055} to FeO_{1.19}. The stoichiometric oxide is thermodynamically unstable with respect to a mixture of metallic iron and FeO_{1.055}. As with ferrous sulphide, the departure from ideal formula arises from the omission of about 5–15 per cent of the cations from the crystal lattice, and the conversion of a corresponding proportion of Fe²⁺ cations to Fe³⁺ cations.²³

Ferrous oxide is of considerable interest in that the variation of composition has been studied under well-defined conditions of equilibrium. There are other examples of transition metal and heavy metal oxide systems in which there is undoubted evidence for the formation of non-stoichiometric compounds, but less certainty that these represent thermodynamically stable species. To this category belong the oxides formed by manganese,²⁴ cobalt,²⁵ nickel,²⁶ uranium²⁷ and lead. Even for so familiar an element as lead, the intermediate oxides formed in the oxidation of PbO and the degradation of PbO₂ present a confused and little-known picture. It is, however, clear that in addition to the well-defined oxide Pb₃O₄, of definite composition, there are at least two non-stoichiometric intermediate phases.²⁸

Some of these compounds, formed as they are by processes of oxidation or degradation at relatively low temperatures, may be metastable, and may break up into stable, stoichiometrically invariable oxides when they are heated to temperatures high enough

²¹ *Z. anorg. Chem.*, 1927, **166**, 113.

²² L. S. Darken and R. W. Gurry, *J. Amer. Chem. Soc.*, 1945, **67**, 1398.

²³ Jette and Foote, *J. Chem. Physics*, 1932, **1**, 29.

²⁴ C. B. Holtermann, *Ann. Chim.*, 1940, **14**, 121.

²⁵ M. Le Blanc and E. Möbius, *Z. phys. Chem.*, 1929, A, **142**, 151.

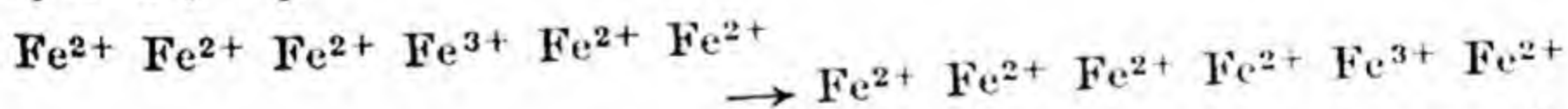
²⁶ M. Le Blanc and H. Sachse, *Z. Elektrochem.*, 1926, **32**, 58, 204; W. Klemm and E. Hass, *Z. anorg. Chem.*, 1934, **219**, 82.

²⁷ W. Biltz and H. Müller, *Z. anorg. Chem.*, 1927, **163**, 257; J. S. Anderson and K. B. Alberman, *J.C.S.*, 1949, S, 303.

²⁸ M. Le Blanc and E. Eberius, *Z. phys. Chem.*, 1932, A, **160**, 69; G. L. Clark and R. Rowan, *J. Amer. Chem. Soc.*, 1941, **63**, 1305; A. Byström, *Arkiv Kemi*, 1945, **20**, A, No. 11; E. Katz., *Ann. Chim.*, 1950, **5**, 5.

to permit of the occurrence of diffusion and recrystallization. This is the case with the lower uranium oxides.

Solid ionic compounds are generally non-conductors of electricity, except at high temperatures when they become ionic conductors through migration of ions within the crystalline solid. Even although in such a compound as chromic oxide, Cr_2O_3 , there are unpaired electrons in the partly filled d levels of the transition metal ions, these electrons are not mobile. In terms of the collective electron model of the solid state, the energy relations are as is represented in Fig. 59D, with a wide energy gap between the occupied energy levels (essentially atomic levels) and the upper band of states in which an electron can migrate from atom to atom through the crystal. The conducting state would correspond to a highly excited state, and the conduction levels are empty in a typical ionic solid at the ordinary temperature. If there is any departure from stoichiometric composition, the foregoing is no longer true. The presence of cations of the same element in different valence states, and in crystallographically equivalent positions, implies that along a lattice row of ions in the crystal there will be points where there is either an excess of electrons (at sites occupied by ions of reduced valency) or a deficit of electrons (at sites occupied by ions of higher valency than those proper to the compounds). Thus along a lattice row of cations in $\text{FeO}_{1.05}$ (which could be written as $(\text{Fe}^{2+}_{0.86}\text{Fe}^{3+}_{0.095})\text{O}^{2-}$), every tenth cation, on the average, is a Fe^{3+} cation, and represents a 'positive hole', or point from which an electron can formally be regarded as lacking. The points of abnormal electron density—the positive holes in the case cited—can move by a process involving only the transference of an electron from one atom to its neighbour, and at each stage the total energy of the system is identical, and represents the lowest energy of the system; *e.g.*



A certain excitation energy may be required, according to the potential barrier to be traversed, but in general the Boltzmann distribution of thermal energies causes a proportion of the electrons or positive holes to be mobile at moderate temperatures, or even at the ordinary temperature. It is therefore characteristic of non-stoichiometric compounds that they are electronic semiconductors. The most minute departure from stoichiometric composition suffices, indeed, to confer a measurable conductivity on otherwise non-conducting compounds. Thus the colour changes produced in ZnO , In_2O_3 , etc., on heating are associated with the reversible loss

of oxygen from the compounds, in the manner considered in a previous paragraph; they are accompanied also by the development of semi-conducting properties. Even the more refractory oxides, such as alumina, become semiconductors of this type at high temperatures, and thus evince some evidence that the view developed above provides a valid model for the equilibrium of a real crystal with its environment. In accordance with the theory, the conductivity of semiconductors of this kind varies systematically with the partial pressure of oxygen (or other component) with which equilibrium is established.

Although minute changes in composition have this effect on the electronic conductivity of ionic solids, particular interest attaches to certain systems in which the concentration of potentially mobile electrons becomes comparable with the number of cations in the system. Such a substance should approximate in certain respects to the properties of a metal. By reason of its unique structure, this is true for example of the spinel Fe_3O_4 , which has a conductivity comparable with that of metals, and several orders of magnitude higher than that of Mn_3O_4 or Ni_3O_4 , which differ in their structure.²⁹ The same unusual character is found in certain derivatives of the intermediate oxides of tungsten, the tungsten bronzes. Because of the fuller study these have received, and the manner in which they may be correlated with the crystal chemistry and general chemistry of the heavier transition elements, these compounds justify a fuller discussion.

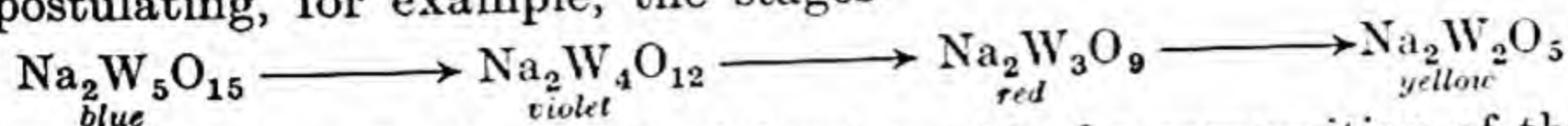
The Tungsten Bronzes and Tungsten Oxides.—It was discovered by Wöhler in 1824 that the reduction of acid sodium tungstate by means of hydrogen at a red heat yielded a chemically inert substance with a metallic, bronze-like appearance. Similar products have since been obtained by numerous workers by heating various mixtures of sodium, potassium or alkaline earth tungstates or polytungstates in hydrogen, by electrolytic reduction of the fused salts, and by the reduction of sodium tungstate with tungsten or sodium in an inert atmosphere. The products of these reactions vary in colour and composition, according to the conditions of reduction,³⁰ but can all be represented by the general formula $\text{R}_2\text{O} \cdot n\text{WO}_3 \cdot \text{WO}_2$, where $n \leq 1$.

These so-called tungsten bronzes are intensely coloured, extremely inert substances with semi-metallic properties: their density is high, and they are good conductors of electricity.

²⁹ Verwey and Haaymann, *J. Chem. Phys.*, 1947, 15, 174, 181.

³⁰ See Mellor, *Comprehensive Treatise*, Vol. XI, p. 750; Spitzin and Kashtanoff, *Z. anorg. Chem.*, 1925, 148, 69; 1926, 157, 141; Engels, *ibid.*, 1903, 37, 125.

The earlier workers attempted to correlate the variations in the colour of the tungsten bronzes with definite ratios of $R_2O : WO_3$, postulating, for example, the stages



The variation of colour and of density with the composition of the bronzes is, however, quite continuous, and provides no evidence for the occurrence of distinct stages in the reduction process. It has been shown by Hägg³¹ that variability of composition is, indeed, an essential characteristic of the compounds. The sodium bronzes Na_xWO_3 , where x varies from 0.95 to 0.30, all crystallize in the cubic system, and the change in colour as x decreases is paralleled exactly by a shrinkage of the crystal cell which brings about the observed changes in the density of the compounds (Table 3).

Table 3

Na_xWO_3	$x = 0.93$	golden-yellow	$a = 3.850 \text{ \AA.}$
	0.64	orange-red	3.834
	0.46	red-violet	3.825
	0.32	dark blue-violet	3.813

It seems that $Na_{0.81}WO_3$ is the bronze richest in sodium that can be prepared by direct reduction, since this co-exists with sodium tungstate in equilibrium studies of the reduction process.³² Thus mixtures with the composition $Na_2WO_4 + xWO_3$ yield mixtures of this bronze and sodium tungstate on reduction if x is less than 1.4, whereas if x is 1.4–4, controlled reduction may convert the mixture to a lower bronze, as the only product—*e.g.* $Na_{0.67}WO_3$ is obtained from $Na_2WO_4 + 2WO_3$. The lower limit of existence of the cubic tungsten bronzes is close to $Na_{0.32}WO_3$.

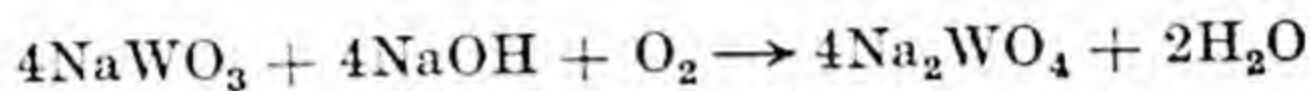
If the substances are considered as solid solutions, it is evident that one end member of the series should be $NaWO_3$, containing quinquevalent tungsten. In practice, this ideal composition may be incapable of attainment, but bright yellow bronzes approaching it can be prepared by the action of sodium on the lower bronzes. The lower limit of the solid solutions would be a non-existent cubic form of WO_3 . Since neither end member of the 'solid solutions' has any certain existence, this terminology is better avoided, the compounds being regarded as a non-stoichiometric phase as in the chemistry of intermetallic phases. The actual cubic tungsten bronzes are derived from the ideal perovskite structure of $NaWO_3$.

³¹ *Nature*, 1935, 135, 874; *Z. physikal. Chem.*, B, 1935, 29, 192.

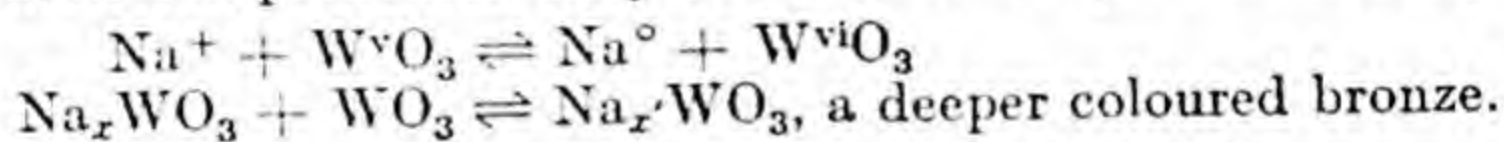
³² D. van Duyn, *Rec. Trav. Chim.*, 1942, 61, 667; R. Schenck and I. Rabes, *Z. anorg. Chem.*, 1949, 259, 201.

by the simple omission of sodium ions from the crystal lattice. A corresponding number of W^{5+} ions are raised to the sexavalent state, W^{6+} , in order to preserve the equivalence of the total anionic and cationic charges, and it is to the simultaneous presence of tungsten in the quinquivalent and sexavalent states that the deep colour of the compounds is due. The association of a deep colour with the presence of the same element in two valency states is a well-known phenomenon which is referred to in several other places in this book.

The conversion of the bronzes into materials richer or poorer in sodium, and most of the chemical reactions of the compounds, turn upon the remarkable mobility of sodium in the crystal lattice.³³ They are insoluble in water and resistant towards acids, being readily attacked only by hydrofluoric acid. They are, however, rather easily oxidized to tungstates, even by atmospheric oxygen—*e.g.*



They are able to reduce ammoniacal silver nitrate to metallic silver. At elevated temperatures they react as if subject to the equilibria



Just as, in the presence of free sodium, the lower bronzes are converted to compounds closer in composition to $NaWO_3$, so acceptors for sodium, such as iodine or WO_3 itself, can abstract sodium and degrade $NaWO_3$ progressively. The transference of sodium from tungsten bronze to acceptor or vice versa may take place through the gaseous phase, but the high diffusion coefficient of sodium within the crystal lattice of the tungsten bronzes enables the reaction to take place progressively and homogeneously throughout the mass.

By using iodine to degrade the bronzes progressively, Straumanis has been able to investigate the compounds Na_xWO_3 over almost the entire range $x = 1$ to $x = 0$. The essential structure throughout is built up of WO_6 octohedra, linked by sharing their vertices with adjacent WO_6 octohedra, and so constituting a skeleton with the composition WO_3 and an anionic charge. In the interstices of this skeleton, the sodium atoms are located. The ideal $NaWO_3$ therefore has the perovskite structure typical of ABO_3 compounds in which the ions A, B and O^{2-} have the appropriate sizes. This cubic crystal lattice remains stable even although up to approximately 70 per cent of the sodium positions are vacant, although the removal of sodium causes a progressive shrinkage. If more than 70 per cent of the sodium ions are dropped out, the distortion is

³³ M. E. Straumanis, *J. Amer. Chem. Soc.*, 1949, 71, 679.

such as to destroy the cubic symmetry, and tungsten bronzes crystallizing in lower crystal systems are obtained. It is evident that the hypothetical lower limit of the series would have the composition WO_3 , containing only hexavalent tungsten, and would possess the crystal structure observed in ReO_3 . There is octahedral co-ordination of oxygen atoms round the tungsten in tungstic oxide itself, and the cell dimensions are similar to those of ReO_3 or the tungsten bronzes, but the WO_6 octahedra are distorted, so that WO_3 crystallizes in the triclinic system.

There is, however, a continuity of structure throughout the series, and the bronzes for which x is less than about 0.3 show a progressive lowering of symmetry. At about $x = 0.2\text{--}0.3$, a tetragonal series of blue tungsten bronzes is formed, from which sodium can be further abstracted, down to the composition $\text{Na}_{0.07}\text{WO}_3$ before any new phase appears. This and the substances still poorer in sodium (e.g. $\text{Na}_{0.03}\text{WO}_3$) appear to have very unusual properties for ternary oxides, for they can be sublimed without change. Their diffraction patterns are similar to that of WO_3 , but they unquestionably contain sodium and quinquevalent tungsten built into their structure. They may, perhaps, be correlated with the complex intermediate oxides formed in the reduction of WO_3 and MoO_3 .

We cannot assign the W^{5+} and W^{6+} ions to definitely different positions in the crystal lattice, but must assume that all the tungsten atoms are equivalent. The extra valency electron carried by the W^{5+} ion is distributed statistically throughout the crystal lattice in exactly the same manner as are the valency electrons of a metallic crystal, thereby conferring on the tungsten bronzes their metallic optical properties and electrical conductivity. The W^{5+} and W^{6+} ions thus become equivalent by a process of resonance.

The intermediate oxides formed in the reduction of WO_3 to WO_2 have long been in question. Although the limiting tungsten bronze, NaWO_3 , should formally be derived from an oxide W_2O_5 , Wöhler³⁴ found that the oxide regarded as W_2O_5 invariably contained more oxygen than accords with that formula. Van Liempt³⁵ assigned to it the formula W_4O_{11} , whilst equilibrium studies in the degradation of WO_3 (Schenck and Rabes³²) clearly point to W_3O_8 . The work of Glemser and Sauer³⁶ suggests that these discrepancies can be harmonized in part, and that it is possible to distinguish four oxides, of which the two intermediate phases, at least, have perceptible ranges of homogeneity. These are α -phase, WO_3 , β -phase, $\text{WO}_{2.92}\text{--}\text{WO}_{2.88}$, γ -phase, $\text{WO}_{2.76}\text{--}\text{WO}_{2.65}$, δ -phase, WO_2 .

³⁴ *Z. Elektrochem.*, 1932, 38, 809 and earlier papers.

³⁵ *Rec. trav. Chim.*, 1931, 50, 343.

³⁶ *Z. anorg. Chem.*, 1943, 257, 144.

The γ -phase thus embraces the compositions assigned to it both by van Liempt and by Schenck and Rabes. It is, however, noteworthy that in the comparable molybdenum oxide system the intermediate oxides have fixed, although unusual, compositions— Mo_8O_{23} , Mo_9O_{26} , Mo_4O_{17} .

Whilst these may be the stable oxide phases, the reduction of WO_3 by hydrogen displays some features of peculiar interest. Reduction by carbon monoxide or hydrogen at 800° yields the violet γ -oxide, but it was found by Ebert and Flasch³⁷ that when tungstic oxide was reduced at the ordinary temperature with atomic hydrogen, the product was a violet oxide, having the same reducing power as authentic W_4O_{11} , but differing in crystal structure.

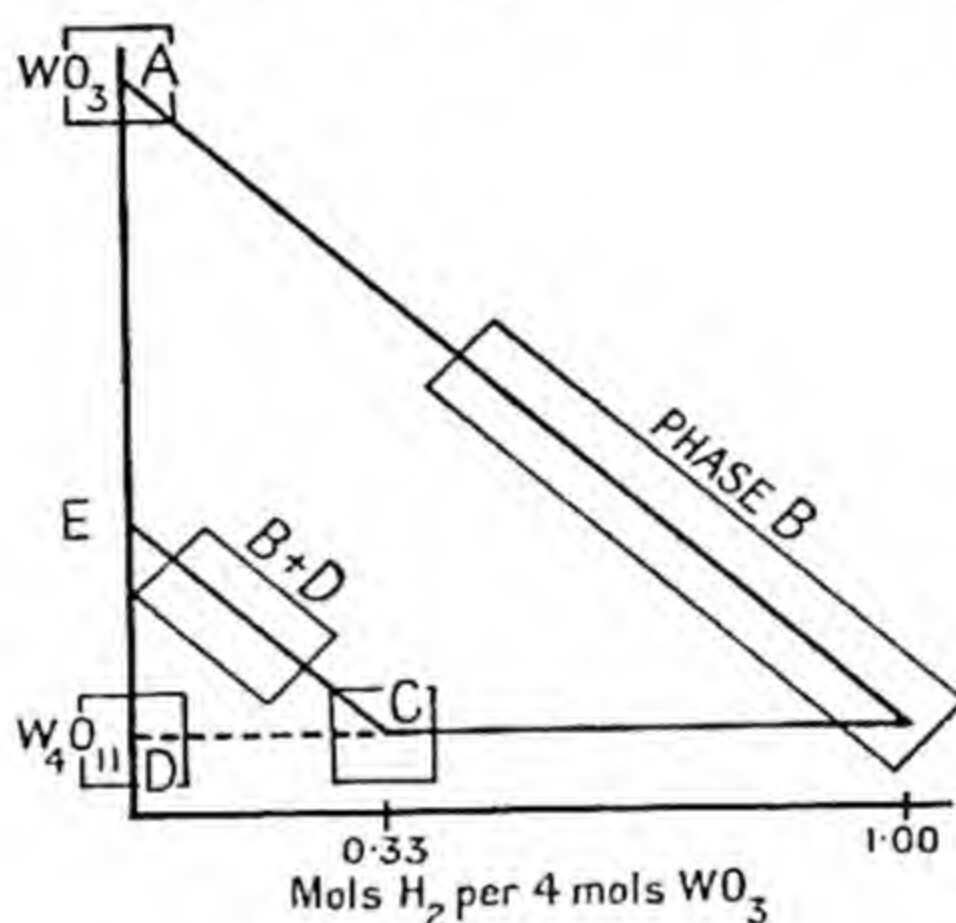


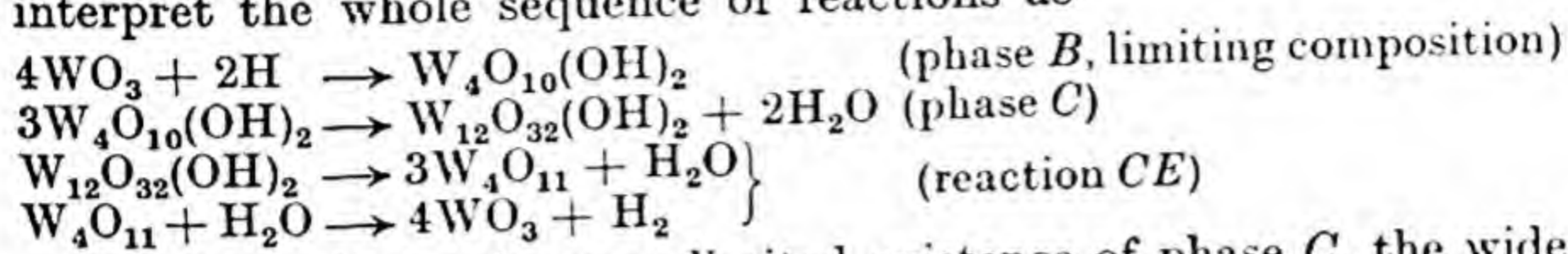
FIG. 66.

The compound formed with atomic hydrogen was shown to contain hydrogen, and to have the composition $\text{W}_4\text{O}_{10}(\text{OH})_2$. It represents the first stage in the reducing action of atomic hydrogen as the direct addition of hydrogen to tungstic oxide.

The degradation of this hydroxide by heat is very interesting. Between 100° and 500° , exactly two-thirds of the combined water is lost (Fig. 66), whereby a new phase *C* is formed, having the composition $\text{W}_{12}\text{O}_{32}(\text{OH})_2$. The continued simple dehydration of this would yield W_4O_{11} (phase *D*); above 500° , however, hydrogen is evolved as such, the final product, *E*, being a mixture of WO_3 and W_4O_{11} . At intermediate stages between *A* and *B*, the phase *B* is present over a wide range as a homogeneous, but not stoichiometric, phase. During the final degradation process *CE*, Ebert and Flasch identified the products, by X-ray analysis, as containing the

³⁷ *Z. anorg. Chem.*, 1934, 217, 95; 1935, 226, 65.

phase $B + W_4O_{11}$ but, remarkably enough, neither the phase C (supposedly $W_{12}O_{32}(OH)_2$) nor free tungstic oxide, WO_3 . Considerable doubt is thrown thereby on the existence of $W_{12}O_{32}(OH)_2$ as a separate entity. Ebert and Flasch, however, regard the phase B as a mixed crystal phase of WO_3 with $W_4O_{10}(OH)_2$, and interpret the whole sequence of reactions as



The facts cited—the very limited existence of phase C , the wide range of existence and reappearance of phase B where phase C should be found, and the non-formation of WO_3 along the reaction line CE —make this interpretation dubious. As Ebert and Flasch have pointed out, phase B can be regarded, non-committally, as a phase of variable composition $W_4O_{12 \cdot n}H_2$, where $n < 1$. The possibility is not excluded that this may be strictly the hydrogen analogue of the tungsten bronzes; such a compound might well degrade by reduction of the tungsten below 500° , and simultaneous reducing action and direct loss of hydrogen at higher temperatures.

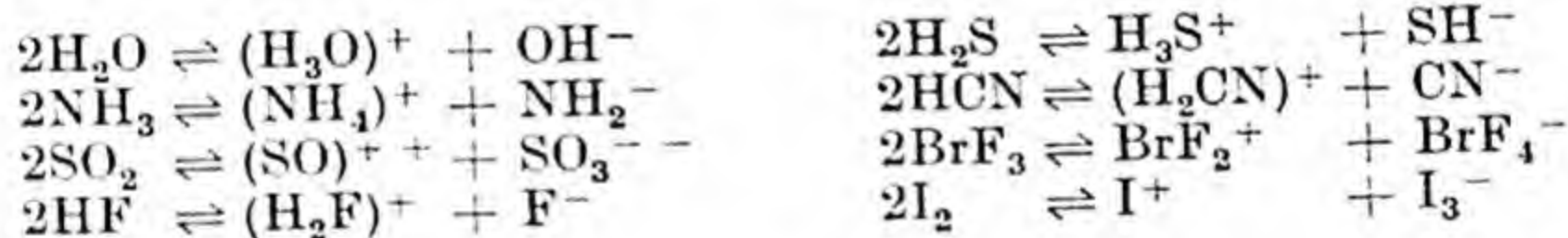
This view has been endorsed by Glemser and Sauer, who observed that although, as stated, WO_3 is reduced by hydrogen at 800° to the β - or γ -oxide under controlled conditions, H_2WO_4 is not merely more readily reduced, but furnishes reduction products quite distinct in colour and diffraction pattern from the β - and γ -oxides. Two substances, designated as phases C_1 , C_2 , were recognized. When heated in argon at 750° , C_2 is converted to C_1 , and the latter in turn to the γ -oxide at 1000 – 1300° . Drastic reduction converts both C_1 and C_2 to the γ -oxide and ultimately to WO_2 . The composition of C_1 and of C_2 is close to that of the γ -oxide, but both contain the elements of water. Part of this is very firmly bound, the last portions (0.5 per cent) being lost only at temperatures approaching 1000° , in the course of conversion to γ -oxide. Glemser and Sauer identify these substances tentatively with the phases B and C of Ebert and Flasch, though this is not proved. The diffraction pattern of C_1 has been interpreted as that of a cubic structure, and the cell dimensions are not very different from those of the tungsten bronzes ($a = 3.75 \text{ \AA}$). If this is confirmed, it can be regarded as the hypothetical cubic WO_3 , but stabilized by the loss of oxygen and presence of hydrogen. The relationship of such a substance to the tungsten bronzes would be close, although as in other quasi-oxyacid systems (*e.g.* the silicates) it must be assumed that hydrogen is present in a localized OH^- ion, and not freely mobile as are the cations of the tungsten bronzes.

CHAPTER XVII

REACTIONS IN LIQUID AMMONIA AND OTHER NON-AQUEOUS MEDIA

The chemist is so familiar with water as a medium in which to study ionic reactions that he tends to overlook other possible solvents. There are, however, a number of alternatives. Of these liquid ammonia has been the most fully investigated,¹ but liquid sulphur dioxide, anhydrous hydrogen fluoride, hydrogen sulphide, hydrogen cyanide, bromine trifluoride, iodine and other substances can all function as ionizing solvents.

The property common to water and the other systems mentioned is that of ionizing to a certain extent when in the pure state, and, as a result, of conducting electricity. The most probable modes of ionization are shown below: they will serve as examples.



In these equations the hydrogen ion derived from water has been represented as associated with a water molecule, forming the ion $(\text{H}_3\text{O})^+$. The counterpart of this ion in liquid ammonia is the ammonium ion $(\text{NH}_4)^+$, while that of hydroxyl is the $(\text{NH}_2)^-$ ion. In liquid sulphur dioxide the thionyl ion, $(\text{SO})^{++}$, is the cation and $(\text{SO}_3)^{--}$ the anion. Similar analogies with water hold throughout the series. As will be seen when these systems are discussed in greater detail, substances which dissolve and ionize to give the cation characteristic of the solvent may be regarded as analogous to acids in the water system. Similarly if the solute yields the anion of the solvent it will function as a base. For example,

¹ Much of the information on liquid ammonia as a solvent given in this chapter is derived from E. C. Franklin's admirable monograph *The Nitrogen System of Compounds* (American Chemical Society Monographs Series, No. 68). A more recent review of the field is given in G. Jander's book, *Die Chemie in Wasserähnlichen Lösungsmitteln* (Springer-Verlag, 1949). See also Watt, *Chem. Rev.*, 1950, 46, 289.

solutions of ammonium salts in liquid ammonia will be analogous to acids in water, while metal amides will correspond to bases.

	Water	Liquid Ammonia
Acids	$\text{HCl} \rightleftharpoons \text{H}^+ + \text{Cl}^-$	$\text{NH}_4\text{Cl} \rightleftharpoons \text{NH}_4^+ + \text{Cl}^-$
Bases	$\text{KOH} \rightleftharpoons \text{K}^+ + \text{OH}^-$	$\text{KNH}_2 \rightleftharpoons \text{K}^+ + \text{NH}_2^-$

Liquid Ammonia.—The solvent action of liquid ammonia extends to a remarkably large number of inorganic substances.² The alkali metals dissolve readily and may be recovered unchanged. On keeping solutions of rubidium and caesium, however, the amides are formed slowly. The alkaline earth metals also dissolve, but the residue on evaporation of the solvent consists of the ammoniates $\text{Ca}(\text{NH}_3)_6$, $\text{Sr}(\text{NH}_3)_6$ and $\text{Ba}(\text{NH}_3)_6$. Most ammonium salts are freely soluble and metal amides are moderately soluble. Among other metallic salts, a few chlorides (*e.g.* NaCl , BeCl_2) are soluble, bromides are as a rule more soluble than chlorides and the majority of metallic iodides are more or less soluble. Most fluorides are insoluble, as are oxides, hydroxides, sulphates, carbonates, phosphates and, in general, sulphites. Nitrates, nitrites, cyanides and thiocyanates on the other hand are mostly soluble. A number of inorganic substances undergo solvolysis with liquid ammonia, *i.e.* react with the solvent.

The solubility of organic compounds in liquid ammonia has also been extensively studied. The paraffin hydrocarbons are almost insoluble at -33° , and aromatic hydrocarbons have a low solubility. Among the readily soluble substances are certain alcohols and phenols, halogen derivatives of aliphatic hydrocarbons, ethers, esters, and many ketones, amines, nitro compounds and sulphonic acids.

It is convenient at this point to interpose a few words about the type of apparatus which is commonly used in studying reactions in liquid ammonia.³ The boiling-point of the pure compound is -33.5° , so that it is necessary to work at low temperatures if relatively high pressures are to be avoided. Liquid ammonia is available commercially in cylinders and can be drawn off into vacuum-jacketed vessels of various types. Treatment with sodium or potassium, followed by distillation, affords a ready means of rendering it anhydrous.

When reactions between liquid ammonia solutions at low temperatures are to be examined, the solutions are often prepared separately, in the two limbs of an inverted U-tube, and then mixed by tilting. The ammonia is readily removed from the reaction

² Cady, *J. Phys. Chem.*, 1897, 1, 707. Franklin and Krause, *Amer. Chem. J.*, 1898, 20, 820. Franklin, *op. cit.*, p. 19.

³ For a detailed description of techniques, see Franklin, *op. cit.*, p. 317.

product by evaporation. Certain reactions have also been studied in sealed tubes under pressure. Similar methods are available for sulphur dioxide (b.p. -10.0°). Measurements of electrical conductivity may be made in apparatus of the usual type placed in a suitable low temperature bath.

The ionic reactions taking place in liquid ammonia are similar in many respects to those which occur in water, but some striking anomalies exist owing to differences in the solubility in the two solvents. Thus, for example, if liquid ammonia solutions of calcium nitrate and sodium chloride are mixed, a precipitate of calcium chloride forms because this is insoluble in liquid ammonia. Chlorides of several other metals may be precipitated in the same way from solutions of nitrates by the addition of ammonium chloride. These are true ionic reactions. Liquid ammonia solutions of ammonium bromide, iodide, chromate or borate give similar precipitation reactions with solutions of the nitrates of a number of metals. Ammonium sulphide, dissolved in liquid ammonia, is also a useful reagent, and will precipitate the sulphides of the alkaline earth metals, magnesium, zinc, manganese, nickel, cobalt, cadmium, lead, silver, mercury, bismuth and copper from nitrate solutions. Some of these sulphide precipitates are identical with those obtained from aqueous solution, but in the case of magnesium the precipitate has the composition $2\text{MgS} \cdot (\text{NH}_4)_2\text{S} \cdot 9-10\text{NH}_3$.

Solutions of Metals in Liquid Ammonia.—The alkali metals give blue solutions in liquid ammonia which conduct electricity well. In dilute solutions of the alkali metals it is believed that the positive ion is that of the metal and the negative ion a negatively charged ammonia molecule or group of such molecules.⁴

The alkali metal solutions are fairly stable but the change to metal amide and hydrogen ($2\text{M} + 2\text{NH}_3 = 2\text{MNH}_2 + \text{H}_2$) is strongly catalysed by certain metals and metallic oxides (*e.g.* Pt, Fe, Fe_2O_3) and also by exposure to ultra-violet light of wavelengths between 2150 and 2550 Å.⁵ The alkali and alkaline earth metals are also soluble in certain amines of low molecular weight, but reaction with the solvent takes place more readily than in the case of ammonia, the products being hydrogen and the substituted metal amide.

The reactions of metal solutions in liquid ammonia have been extensively studied.⁶ Typical instances of the reactions with elements are shown in Table 1.

⁴ Jander, *op. cit.*, p. 47.

⁵ Ogg, Leighton and Bergstrom, *J. Amer. Chem. Soc.*, 1933, 55, 1754.

⁶ See Fernelius and Watt, *Chem. Reviews*, 1937, 20, 195. This section is largely based on this review.

Table 1

Element	Metal	Products
O . . .	Na	Na_2O_2
	Ba	BaO ; BaO_2
S . . .	Li	LiS , Li_2S_2 . . . Li_2S_x
Se . . .	Na	Na_2Se , Na_2Se_2 . . . Na_2Se_6
Te . . .	K	K_2Te , K_2Te_3
P . . .	K	KP_5 , 3NH_3
As . . .	K	K_2As , 3NH_3 ; K_2As_4 , NH_3
Sb . . .	Na	$\text{Na}_3\text{Sb}_{5-7}$
Pb . . .	Na	NaPb ; NaPb_2 ; Na_4Pb_9

The reaction with metal halides leads either to the formation of the free metal or of an intermetallic compound ⁷ (e.g. $\text{CuI} + \text{Na} \rightarrow \text{Cu}$; $\text{ZnI}_2 + \text{Na} \rightarrow \text{NaZn}_4$). These intermetallic compounds are similar to those discussed in Chapter XV. Their constitution is not governed by the normal valencies of the elements concerned.

Among the other reactions of these metal solutions in ammonia those with carbon monoxide yield a series of unstable derivatives of hexahydroxy benzene (e.g. $\text{C}_6(\text{OK})_6$).⁸ With nitric oxide the compounds NaNO , KNO , and $\text{Ba}(\text{NO})_2$ have been obtained as gelatinous precipitates.⁹ These formulæ suggest that the compounds are hyponitrites derived from $\text{H}_2\text{N}_2\text{O}_2$, but Zintl and Harder¹⁰ have shown that the sodium derivative $(\text{NaNO})_x$ differs in its X-ray diagram from sodium hyponitrite. It is possible that the compounds are nitroxyls and their structures and reactions would seem to merit further study.

Little is known at present about the reactions of these metal solutions in liquid ammonia with more complex inorganic compounds. The sodium solution when treated with sodium nitrite forms the compound Na_2NO_2 . According to some comparatively old observations by Joannis,¹¹ phosphine reacts with potassium and sodium in ammonia solution to form NaPH_2 and KPH_2 . Monogermane and digermane react similarly with a solution of sodium the products in each case being NaGeH_3 and hydrogen.¹²

⁷ Kraus and Kurtz, *J. Amer. Chem. Soc.*, 1925, 47, 43. Zintl *et al.*, *Z. physikal Chem.*, 1931, A, 154, 1.

⁸ Pearson, *Nature*, 1933, 131, 166.

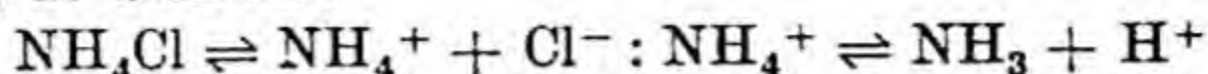
⁹ Joannis, *Ann. Chim. Phys.*, 1906, [8], 7, 84. Mentrel *Compt. rend.*, 1902, 135, 740.

¹⁰ *Ber.*, 1933, 66, 760.

¹¹ *Compt. rend.*, 1894, 119, 557. *Ann. Chim. Phys.*, 1906, [8], 7, 101.

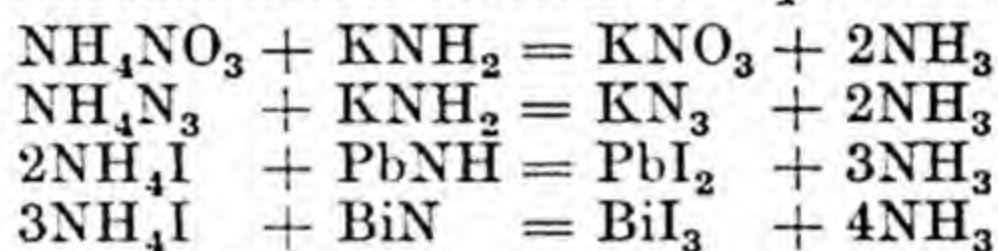
¹² Kraus and Carney, *J. Amer. Chem. Soc.*, 1934, 56, 765.

Ammonium Salts and Amides in Liquid Ammonia.—Salts such as ammonium chloride when dissolved in ammonia increase the conductivity of the pure solvent ($3 \times 10^{-8} \text{ ohm}^{-1} \text{ cm.}^{-1}$ at -37°) by ionizing as follows :



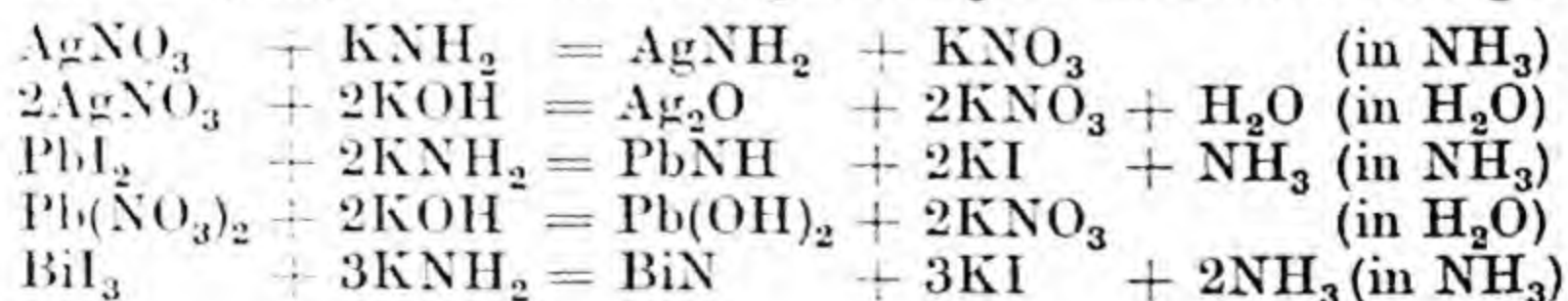
These solutions are sufficiently acid to dissolve a number of metals with liberation of hydrogen. Metallic hydroxides and oxides also dissolve in a concentrated solution of ammonium nitrate in liquid ammonia. The latter is known as Divers' liquid and its solvent action has been known for over seventy years.¹³

Metallic amides, imides and nitrides also react with liquid ammonia solutions of ammonium salts. If the latter are regarded as acids, these reactions, examples of which are given below, are analogous to neutralization reactions in aqueous systems.



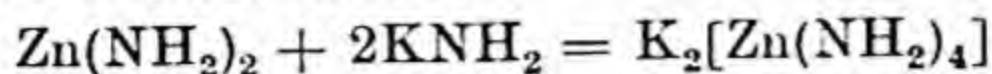
There is a close parallel between the two systems, amides and imides being the counterpart of hydroxides, and nitrides of oxides. These neutralization reactions may be followed by means of conductimetric titrations and also, in a limited number of cases, by means of indicators. A liquid ammonia solution of phenolphthalein, for example, is colourless but develops an intense red colour on the addition of potassium amide. This colour is discharged by adding the requisite amount of a solution of dicyanimide, which is acidic in its behaviour ($\text{KNH}_2 + \text{HN}(\text{CN})_2 = \text{KN}(\text{CN})_2 + \text{NH}_3$). Guanidine, $(\text{NH}_2)_2\text{CNH}$, and cyanamide, $\text{NH}_2(\text{CN})$, also function as acidic substances in ammonia.

Metallic amides, imides or nitrides can be precipitated from liquid ammonia solutions of certain metallic salts by potassium amide, the latter corresponding to potassium hydroxide in the aqueous system. The formation of an imide or nitride in place of an amide corresponds with the partial or total dehydration of a hydroxide precipitated in aqueous solution. The following examples illustrate this point.

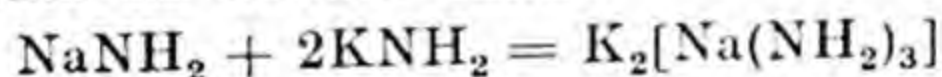


¹³ Franklin, *J. Amer. Chem. Soc.*, 1913, **35**, 1455. Davis, Olmstead and Landstrum, *ibid.*, 1921, **43**, 1583. Bergstrom, *J. Phys. Chem.*, 1925, **29**, 160; *J. Amer. Chem. Soc.*, 1928, **50**, 657. Divers, *Proc. Roy. Soc.*, 1875, **21**, 109.

Alkali Metal Salts of Amphoteric Amides and Imides.—Zinc amide dissolves in an ammonia solution of potassium amide and forms potassium ammonozincate



This is clearly an example of amphoteric behaviour in the ammonia system, the product corresponding to the aquozincate, $\text{K}_2[\text{Zn}(\text{OH})_4]$, produced when zinc hydroxide dissolves in aqueous potassium hydroxide. The ammonia compound is, however, stable in liquid ammonia, whereas the aquo compound is readily hydrolysed. Similar amphoteric behaviour has been observed with a number of other metallic amides. Lead imide, PbNH , for example, is readily soluble in an ammonia solution of potassium amide. The product, which has the composition $\text{PbNK}, 2.5\text{NH}_3$, loses ammonia, progressively forming $\text{PbNK}, 2\text{NH}_3$ (or $\text{K}[\text{Pb}(\text{NH}_2)_3]$) and PbNK, NH_3 . Aluminium amalgam reacts rather similarly with potassium amide forming $\text{K}[\text{Al}(\text{NH}_2)_4]$, which loses ammonia when heated in vacuum at 55° and forms $\text{K}[\text{HN}=\text{Al}(\text{NH}_2)_2]$. Even more striking is the formation of potassium ammonosodiate, $\text{NaNK}, 2\text{NH}_3$ (or $\text{K}_2[\text{Na}(\text{NH}_2)_3]$), by the action of potassium amide in liquid ammonia on sodium amide.



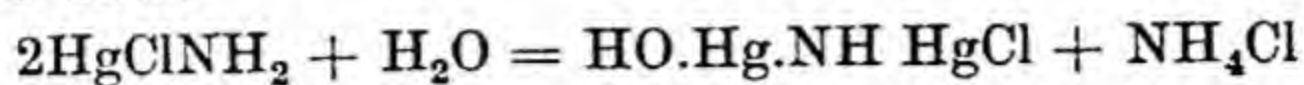
Basic Salts.—The action of water in hydrolysing normal salts to basic salts finds an exact counterpart in the reaction between ammonia and salts of some of the heavy metals. Lead iodide, for example, is fairly soluble in liquid ammonia and from the resulting solution the compound $\text{Pb}(\text{NH}_2)_2 \cdot \text{Pb}(\text{NH}_2)\text{I}$ can be separated. In the same way lead nitrate gives the compound $\text{PbNH} \cdot \text{NH}_2 \cdot \text{PbNO}_3$. When potassium amide is added, more of this compound is deposited, while ammonium nitrate causes it to dissolve, just as a mineral acid will often dissolve a basic salt deposited from water. In these compounds the NH_2 and NH groups fulfil the role of OH and oxygen in aqueous systems.

Franklin has applied these principles to explain the compounds formed between ammonia and the mercuric halides. These he considers as falling into three classes, namely:

- (1) Normal mercury salts with ammonia of crystallization.
- (2) Ammonobasic mercuric salts.
- (3) Mixed aquobasic-ammonobasic mercuric salts.

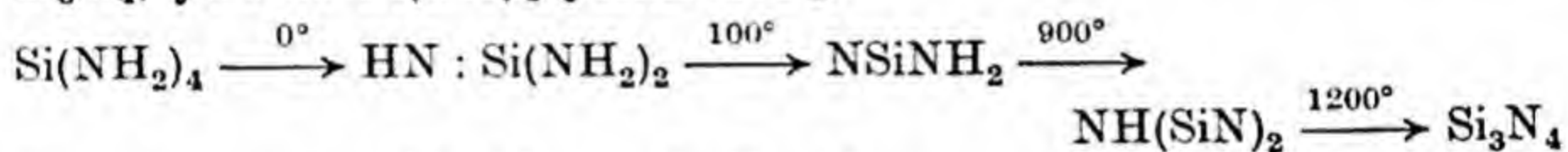
In the first class are salts such as $\text{HgCl}_2, 2\text{NH}_3$ and $\text{HgBr}_2, 2\text{NH}_3$, which are formed by the action of ammonia on the halide in presence of sufficient of an acidic ammonium halide to prevent ammonolysis. The ammonobasic mercuric salts are of the type of infusible white precipitate, HgClNH_2 , one method for forming which is by the

treatment of mercuric chloride with liquid ammonia. Many similar ammonobasic salts have been described. Prolonged treatment of infusible white precipitate with water or aqueous ammonia transforms it to an insoluble yellow substance which is the chloride of Millon's base.

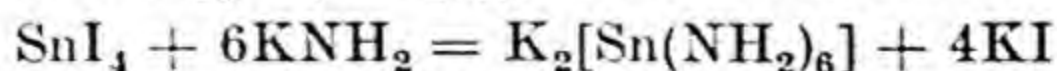


This compound is termed by Franklin a mixed aquobasic-ammonobasic salt. With water or sodium hydroxide hydrolysis proceeds slowly to completion with the formation of mercuric hydroxide, while with ammonium chloride infusible white precipitate is re-formed.

Amides of the Non-Metals.—Reaction between water and halides of the non-metals normally leads to replacement of the halogen by hydroxyl groups. A comparable reaction occurs with ammonia, and from the resulting amides it is in some cases possible to obtain nitrides by heating. A typical reaction is that between silicon tetrachloride and ammonia. The initial product, $\text{Si}(\text{NH}_2)_4$, the analogue of orthosilicic acid, is degraded stepwise by heat to Si_3N_4 , just as $\text{Si}(\text{OH})_4$ yields SiO_2 .



Titanium tetrachloride and liquid ammonia form the amide $\text{Ti}(\text{NH}_2)_4$, which gives the diimide, $\text{Ti}(\text{NH})_2$, on heating. Germanium halides behave rather similarly, the tetraiodide and ammonia forming the imide $\text{Ge}(\text{NH})_2$,¹⁴ which when heated to 150° gives germanam, $(\text{GeN})_2\text{NH}$,¹⁵ the analogue of silicam, $(\text{SiN})_2\text{NH}$, and of cyanimide, $(\text{CN})_2\text{NH}$. Germanam at 350° forms the nitride Ge_3N_4 . With germanous iodide and liquid ammonia, ammono germanous acid, $\text{Ge}=\text{NH}$, is formed as an insoluble yellow powder, analogous to the unknown *iso*-hydrocyanic acid. Practically nothing is known about the possible existence of salts and esters of any of these germanium compounds. A similar state of affairs exists with regard to the reaction of zirconium halides with liquid ammonia: ZrI_4 probably gives the tetra amide.¹⁶ Amides and imides of both stannic and stannous tin should exist, but the only such derivative of tetravalent tin known at present is potassium ammonostannate, $\text{K}_2[\text{Sn}(\text{NH}_2)_6]$, which is formed in the reaction



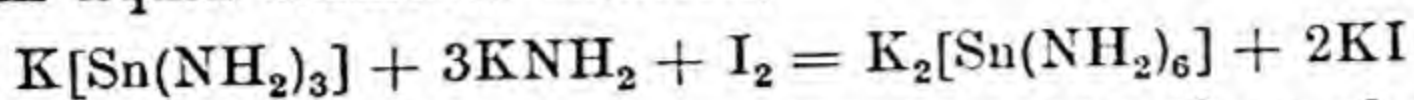
Potassium ammonostannite, $\text{K}[\text{Sn}(\text{NH}_2)_3]$, is formed when tin is

¹⁴ Johnson and Sidwell, *J. Amer. Chem. Soc.*, 1933, 55, 1884.

¹⁵ Schwarz and Schenk, *Ber.*, 1930, 63, 296.

¹⁶ Stähler and Denk, *Ber.*, 1905, 38, 2611.

treated with a solution of potassium amide in liquid ammonia.¹⁷ Oxidation from the di- to the tetravalent condition can be effected by treating the ammonostannite with iodine and excess of potassium amide in liquid ammonia solution,



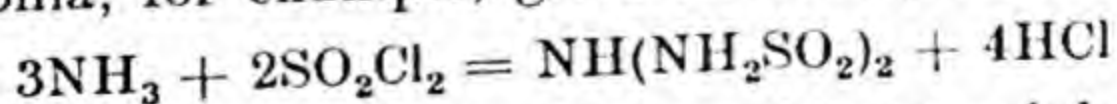
Phosphorus pentachloride and ammonia react to form phosphorus chloronitride (*cf.* p. 350) which on further treatment with ammonia forms phosphoric nitride diamide, $\text{NP}(\text{NH}_2)_2$. This is an acidic substance and, although no salts are known, several esters have been prepared. The compound phospham, $\text{NP}:\text{NH}$, is formed by heating phosphoric nitride diamide. It was known to Davy, who prepared it by heating phosphorus pentachloride with ammonia, and is a white infusible powder which is insoluble in water and dilute acids, but is slowly attacked by aqueous potash. It can be hydrolysed to phosphoric acid and ammonia by heating with water in a sealed tube.

In addition to derivatives containing amino and imino groups a number of phosphorus compounds are known in which both hydroxyl and amino groups are present. These are mixed aquo-ammono phosphoric acids, and although it is not proposed to discuss here their modes of formation and properties, the following formulæ may be quoted as showing how they are related to the phosphoric acids :

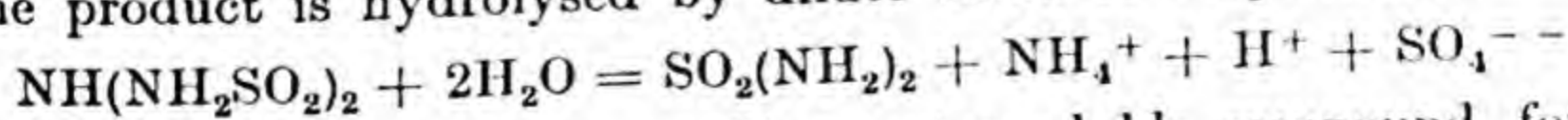
$\text{H}_2\text{NPO}(\text{OH})_2$	amido ortho phosphoric acid
$(\text{H}_2\text{N})_2\text{PO}(\text{OH})$	diamido ortho phosphoric acid
$(\text{H}_2\text{N})_3\text{PO}$	triamido ortho phosphoric acid
$(\text{NH})(\text{H}_2\text{N})\text{PO}$	amido imido ortho phosphoric acid
$(\text{H}_2\text{N})\text{PO}_2$	amido metaphosphoric acid

The halides of trivalent phosphorus give reaction products with ammonia which are similar to those from the pentachloride. Liquid ammonia and phosphorus tribromide, for example, form the triamide $\text{P}(\text{NH}_2)_3$. This loses ammonia at 0° forming the imide $\text{P}_2(\text{NH})_3$. The acids $(\text{H}_2\text{N})_2\text{P}(\text{OH})$, $(\text{H}_2\text{N})\text{P}(\text{OH})_2$ and $(\text{H}_2\text{N})\text{PO}$ are also known.

Sulphur halides and oxyhalides undergo a number of interesting reactions with ammonia. The addition of sulphuryl chloride to liquid ammonia, for example, gives imidosulphamide,



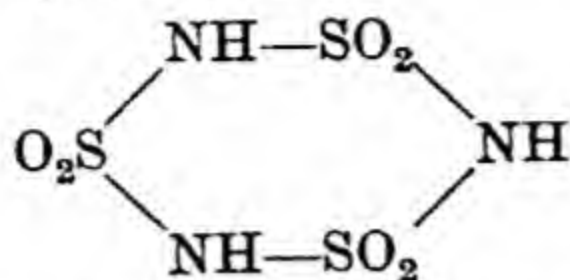
The product is hydrolysed by dilute acids to sulphamide,



Sulphamide, which is a crystalline water-soluble compound, forms

¹⁷ Bergstrom, *J. Phys. Chem.*, 1926, 30, 15.

metallic salts and esters (*e.g.* $\text{SO}_2(\text{NHAg})_2$). When heated, sulphamide forms, among other products, sulphimide, which is trimeric and probably has the cyclic formula

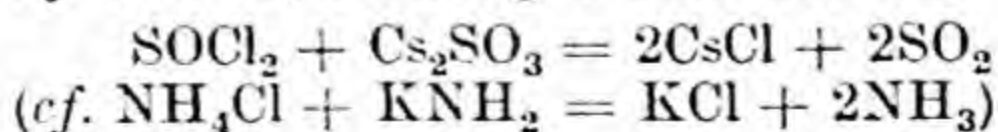


Free sulphimide is known only in aqueous solution and behaves as a moderately strong acid, salts such as $(\text{SO}_2\text{NNa})_3$ and $(\text{SO}_2\text{NAg})_3$ being well established. Up to the present, attempts to prepare compounds such as $\text{S}(\text{NH}_2)_6$, $\text{S}(\text{NH}_2)_4\text{NH}$ or $\text{S}(\text{NH}_2)_2$ from sulphur halides and ammonia have been unsuccessful, but a considerable number of acidic compounds are known in which both hydroxyl and amino groups occur.¹⁸

Chemistry of Liquid Sulphur Dioxide Solutions

It has been known since the early investigations of Walden and Centnerszwer¹⁹ that anhydrous liquid sulphur dioxide (b.p. -10.02°) is a good solvent for a large number of inorganic and organic substances. Many of the resulting solutions conduct electricity, although sulphur dioxide itself has only a low conductivity ($1 \times 10^{-7} \text{ ohm}^{-1} \text{ cm.}^{-1}$ at 0°). This subject has been taken up afresh by Jander and his co-workers²⁰ with the result that chemistry in liquid sulphur dioxide has been placed on much the same footing as that in liquid ammonia. Reference has been made already to the probable mode of ionization of sulphur dioxide, which accounts for its small but definite conductivity ($2\text{SO}_2 \rightleftharpoons \text{SO}^{++} + \text{SO}_3^{--}$).

By analogy with water and ammonia solutions, compounds which dissolve and give the thionyl ion, SO^{++} , should behave as acids in this solvent, while those yielding the sulphite ion, SO_3^{--} , should be bases. Jander has found that thionyl chloride and other thionyl derivatives are in fact freely soluble in liquid sulphur dioxide, and enhance its conductivity. A number of sulphites are also soluble and also increase the conductivity. Ionic reactions between thionyl derivatives and sulphites in liquid sulphur dioxide may be followed conductimetrically and may be regarded as the neutralization of an acid by a base, forming a salt and the solvent: *e.g.*



¹⁸ For a detailed account of these products, see *Systematic Inorganic Chemistry of the Fifth and Sixth Group Nonmetallic Elements*, by D. M. Yost and H. Russell (New York, Prentice-Hall, Inc., 1944).

¹⁹ *Ber.*, 1899, 32, 2862.

²⁰ Jander, *op. cit.*

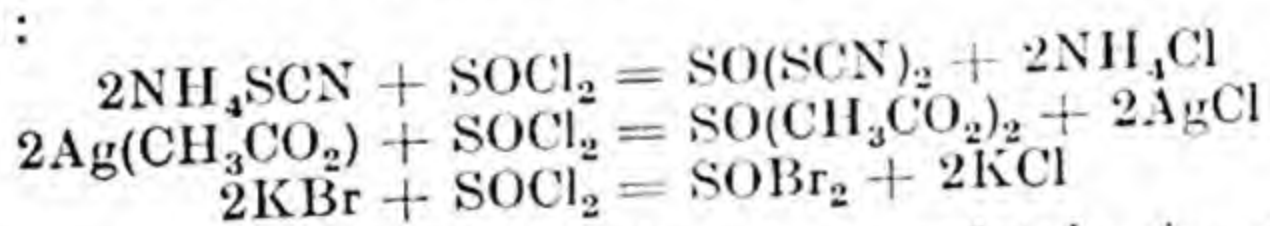
Solubilities in Liquid Sulphur Dioxide.²¹—Solubilities in liquid sulphur dioxide vary considerably. Thus the alkali metal sulphites have solubilities at 0° of the order of 0.02–0.05 g. per 100 g. of SO₂. Tetramethyl ammonium sulphite, on the other hand, is freely soluble, but the sulphites of barium and manganese are insoluble. Thionyl chloride and thionyl acetate are miscible with sulphur dioxide in all proportions.

Alkali and alkaline earth metal iodides are moderately soluble but bromides, chlorides and fluorides become progressively less soluble. Saturated solutions of a number of other inorganic salts have concentrations which range from 10⁻² to 10⁻³ molar. Many oxides, sulphides and hydroxides on the other hand are practically insoluble. Sulphur dioxide is generally a good solvent for organic compounds.

Certain inorganic salts form definite addition compounds which correspond in type to hydrates and ammoniates. As a rule they dissociate readily ($p_{\text{SO}_2} = 1$ atm. at 0–50°). Typical molecular formulæ are shown below: little is yet known about the crystal structures.

NaI, 4SO ₂	LiI, 2SO ₂	LiI, SO ₂	K(SCN), 0.5SO ₂
KI, 4SO ₂	NaI, 2SO ₂	AlCl ₃ , SO ₂	Rb(SCN), 0.5SO ₂
SrI ₂ , 4SO ₂	SrI ₂ , 2SO ₂	K(SCN), SO ₂	Cs(SCN), 0.5SO ₂
BaI ₂ , 4SO ₂	BaI ₂ , 2SO ₂		Ca(SCN) ₂ , 0.5SO ₂

Reactions in Liquid Sulphur Dioxide.—A knowledge of solubility relationships has enabled a number of precipitation reactions to be carried out. This is well illustrated by experiments leading to new thionyl derivatives, in which the following reactions were used:

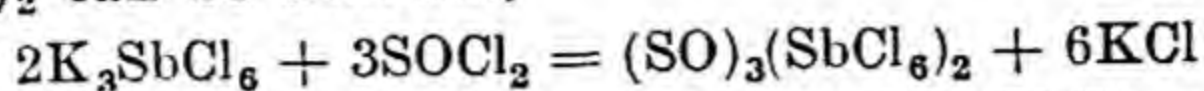


The halides are precipitated almost completely in each case. Thionyl thiocyanate and acetate cannot be isolated in the pure state by evaporating the sulphur dioxide, as they decompose too readily. Thionyl bromide can, however, be prepared in a pure state by the above reaction. Attempts to apply an analogous reaction to the preparation of thionyl iodide have not been successful as the compound decomposes with liberation of free iodine.

There is good evidence for the formation of a number of complex halogen compounds in liquid sulphur dioxide. Thus antimony trichloride and potassium chloride, both of which are soluble, give the complex K₃SbCl₆, while from antimony pentachloride K₃SbCl₆.

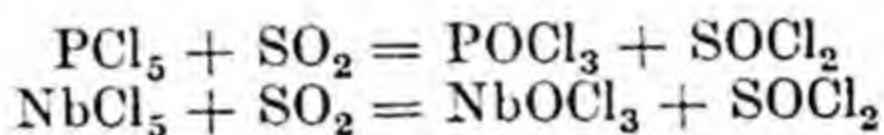
²¹ Jander, *op. cit.*; see also Lauder and Rossiter, *Nature*, 1949, 163, 567.

is obtained. The solubility both of antimony pentachloride and trichloride in sulphur dioxide is enhanced by the addition of thionyl chloride. From the change in conductivity on titrating a solution of K_3SbCl_6 with thionyl chloride formation of the free acid $(\text{SO})_3(\text{SbCl}_6)_2$ can be deduced,

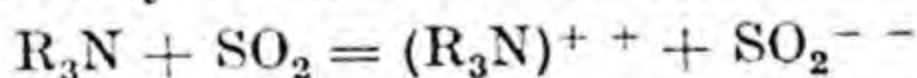


In general, however, such compounds as $(\text{SO})_3\text{SbCl}_6$ are unstable and cannot be isolated in the free state. There is considerable evidence for the formation of other related complexes. Thus aluminium chloride increases the solubility of potassium chloride in sulphur dioxide very greatly, which suggests the formation of a salt such as KAlCl_4 in solution. Aluminium chloride and also the tetrachlorides of silicon, titanium and tin are all much more soluble in sulphur dioxide if thionyl chloride is added. This again indicates that 'acidic' compounds analogous to thionyl hexachloroantimonate may be produced.

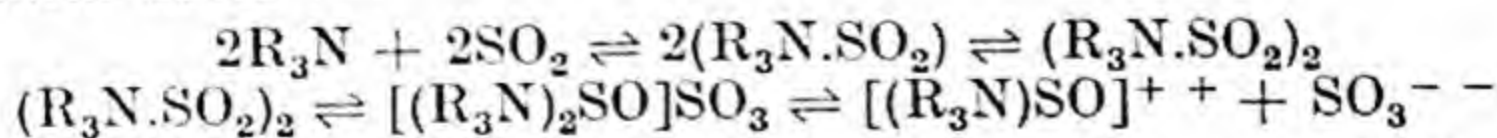
Solvolysis reactions have also been observed in liquid sulphur dioxide. Phosphorus pentachloride, for example, reacts readily to form POCl_3 , while other halides (*e.g.* NbCl_5) react if heated in a sealed tube.



Reaction of Amines with Sulphur Dioxide.—Many amines dissolve readily in liquid sulphur dioxide, forming solutions which conduct electricity. The exact nature of the ions formed is not yet certain. Walden and Centnerszwer²² originally suggested that, in the case of tertiary amines, the reaction



occurred, while Bateman, Hughes and Ingold,²³ from molecular weight and conductivity measurements, have concluded that the ions $(\text{R}_3\text{N})^+$ and SO_2^{--} are present. Jander and his co-workers maintain that the ionic compound $[(\text{R}_3\text{N})_2\text{S}=\text{O}]\text{SO}_3$ is formed. This would be a base in liquid sulphur dioxide, comparable in its constitution and mode of formation with $(\text{R}_3\text{NH})\text{OH}$ in aqueous systems. This formula may be reconciled with the molecular weight and conductivity data if it is assumed that the following equilibria occur:²⁴



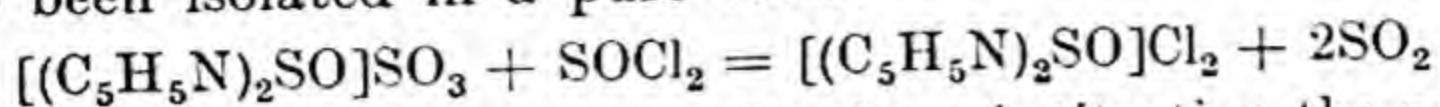
Solutions of organic bases in sulphur dioxide react with thionyl

²² *Z. anorg. Chem.*, 1902, **30**, 145; *Z. physikal. Chem.*, 1903, **43**, 385.

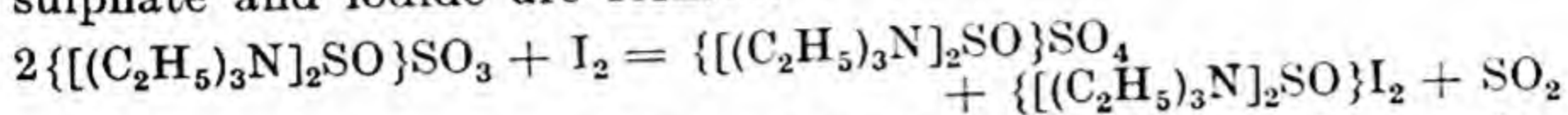
²³ *J.C.S.*, 1944, 243.

²⁴ Jander, *op. cit.*, p. 285 *et seq.*

derivatives. The reaction of pyridine with thionyl chloride, for example, may be followed by a conductimetric titration and appears to occur according to the following equation, though the product has not been isolated in a pure state.

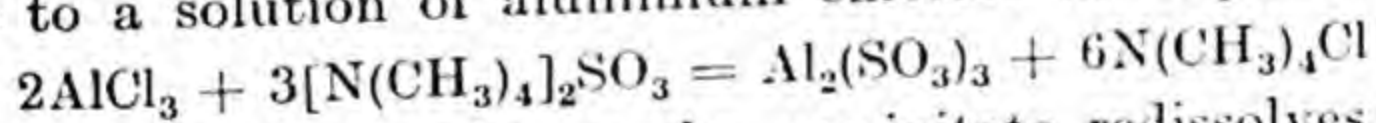


It is also possible to follow by a conductimetric titration the reaction in liquid sulphur dioxide between triethylamine and iodine, in which sulphate and iodide are formed.

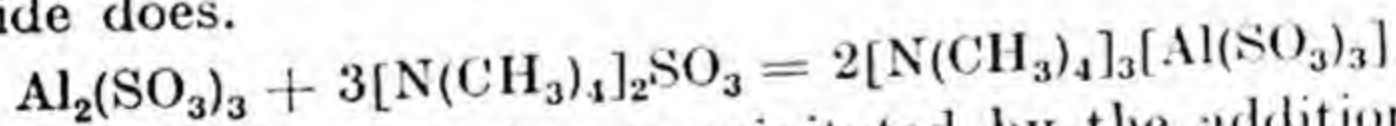


This oxidation process would be difficult to account for if the amine solution did not contain sulphite ions, and, although attempts to isolate salts such as $\{[(C_2H_5)_3N]_2SO\}SO_3$ in the pure state have so far failed, the evidence for their existence in solution is fairly strong. Jander's attempts to formulate the compounds formed by amines and sulphur dioxide as sulphites do, in spite of the strong criticism by Ingold and his co-workers,²⁵ give a unified picture of the field.

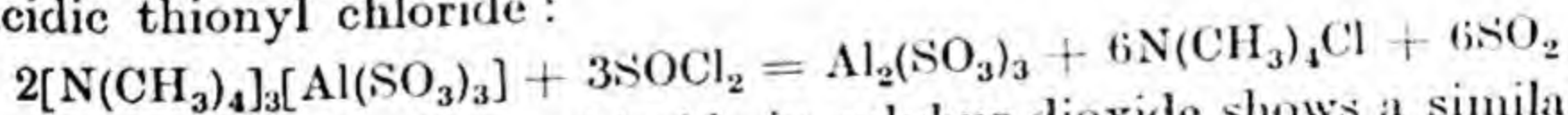
Amphoteric Behaviour in Liquid Sulphur Dioxide.—The amphoteric nature of hydroxides such as those of aluminium and zinc is so well known, that it is a matter of considerable interest to find the counterpart of this behaviour in liquid sulphur dioxide systems. An example is furnished by aluminium sulphite, which is obtained as a white precipitate on adding tetramethyl ammonium sulphite to a solution of aluminium chloride in sulphur dioxide.



On addition of excess of base the precipitate redissolves, though if allowed to stand it ages and becomes less soluble, just as aluminium hydroxide does.



Aluminium sulphite can be reprecipitated by the addition of the acidic thionyl chloride:



A solution of gallium chloride in sulphur dioxide shows a similar behaviour.²⁶

Other Non-Aqueous Systems

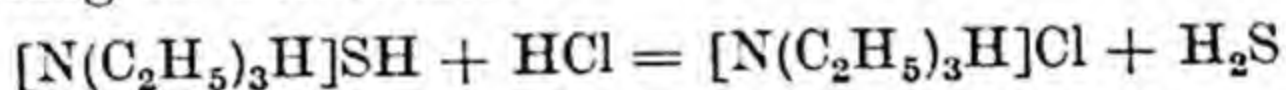
Hydrogen Sulphide.—The conductivity of liquid hydrogen sulphide (b.p. -61°) is very low (3.7×10^{-11} ohm⁻¹ cm.⁻¹ at

²⁵ See Ref. 23.

²⁶ For other examples, see Jander, *op. cit.*, p. 278 *et seq.* The evidence for amphoteric behaviour is not in every case convincing.

— 78.3°).²⁷ Assuming that the ionization is similar to that of water, ($2\text{H}_2\text{S} \rightleftharpoons (\text{H}_3\text{S})^+ + (\text{SH})^-$), one would expect solutes yielding hydrogen ions to be analogous to acids and those yielding the $(\text{SH})^-$ ion to function as bases. A number of acids (*e.g.* HCl , HBr , H_2SO_4 , $\text{CH}_3\text{CO}_2\text{H}$, $\text{CCl}_3\text{CO}_2\text{H}$) are soluble, and although metallic sulphides in general are insoluble, aryl- and alkyl-substituted ammonium sulphides and hydrosulphides (*e.g.* $[\text{NH}(\text{C}_2\text{H}_5)_3]\text{SH}$) are readily soluble. In addition, a number of halides (*e.g.* ZnCl_2 , HgCl_2 , AlCl_3 , FeCl_3 , CCl_4 , SiCl_4 , SnCl_4 , PCl_3 , AsCl_3 , S_2Cl_2) also dissolve, as do numerous organic substances.²⁸

Recently the scattered references in the literature to solutions in liquid hydrogen sulphide have been brought together by Jander.²⁹ Many dissolved substances enhance the conductivity of the solvent and it has been shown by conductimetric titrations that neutralization reactions between the analogues of acids and bases can occur. For example, when dry hydrogen chloride is passed from a gas burette into a suspension of the sparingly soluble triethyl ammonium hydrosulphide in hydrogen sulphide there is a sharp break in the conductivity-HCl concentration curve at an equivalence point corresponding to the reaction



A number of indicators give sharp colour changes in passing from the 'acid' to the 'alkaline' region in hydrogen sulphide. Jander has also established qualitatively, from observations on the behaviour of metals when placed in sealed tubes with hydrogen sulphide at room temperature, an electrochemical series analogous to that in water.

Two further points of analogy with aqueous systems remain to be mentioned. The first, solvolysis, occurs in many instances. The following are examples of compounds which react either at — 78° or at room temperature.³⁰

Compound	Product of Solvolysis
Hg_2Cl_2	$\text{Hg}_2(\text{SH})_2 + \text{HCl}$
HgCl_2	$\text{HgS} + \text{HCl}$
SnCl_4	SnS_2 (slow)
PCl_5	PSCl_3
AsCl_3	As_2S_3
$\text{CH}_3\text{CO}(\text{SCH}_3)$	$\text{CH}_3\text{CO}(\text{SH}) + \text{CH}_3(\text{SH})$

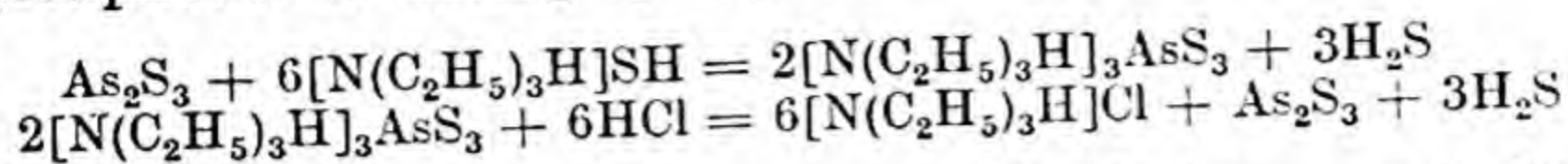
²⁷ Satwalekar, Butler and Wilkinson, *J. Amer. Chem. Soc.*, 1930, **52**, 3045.

²⁸ Quam, *ibid.*, 1925, **47**, 103. Biltz and Keuneeke, *Z. anorg. Chem.*, 1925, **147**, 171. McIntosh and Archibald, *Z. physikal. Chem.*, 1906, **55**, 152.

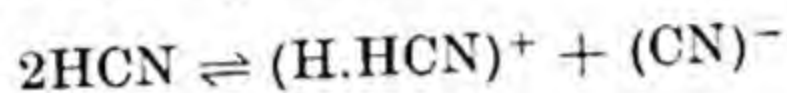
²⁹ Jander, *op. cit.*, p. 77. Jander and Schmidt, *Wiener Chemiker Ztg.*, 1943, **46**, 49.

³⁰ Ralston and Wilkinson, *J. Amer. Chem. Soc.*, 1928, **50**, 258, 2160.

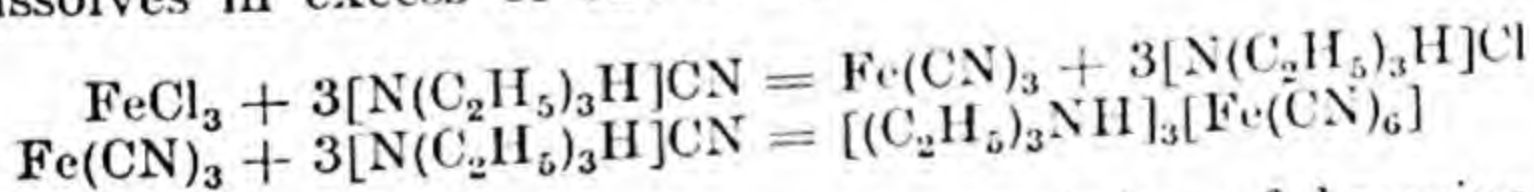
The second point, amphoteric behaviour, is well illustrated by the behaviour of arsenic trisulphide, which dissolves readily in a solution of triethylammonium hydrosulphide (a 'base') and is reprecipitated on adding hydrogen chloride,



Hydrogen Cyanide.—The chemistry of solutions in anhydrous hydrogen cyanide (b.p. 25°) is very similar to that in hydrogen sulphide.³¹ The pure compound has a low conductivity ($5 \times 10^{-7} \text{ ohm}^{-1} \text{ cm.}^{-1}$), but is an excellent solvent. Many of the resulting solutions conduct electricity (*e.g.* those of many salts of the alkali metals, of certain non-metallic halides and of a limited number of organic substances). The ionization of the pure solvent occurs according to the equation:



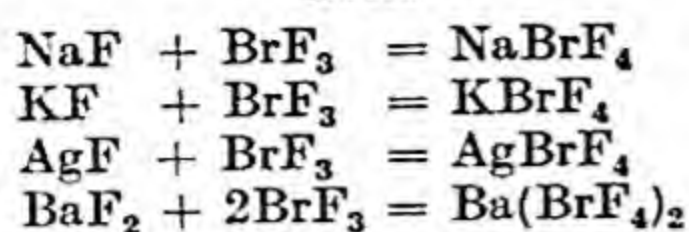
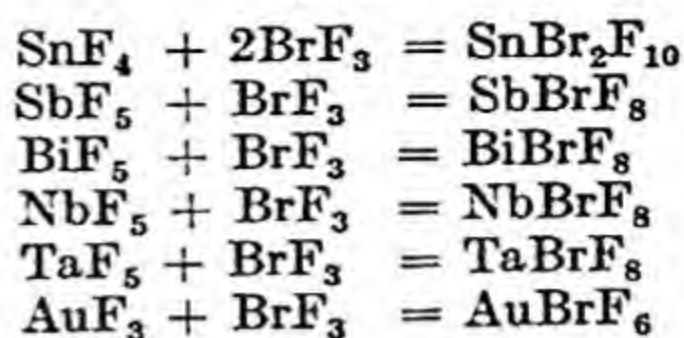
On the basis already explained, soluble acids (*e.g.* H_2SO_4 , HNO_3 , HCl , picric acid) function as 'acids' and compounds capable of furnishing cyanide ions (*e.g.* alkali metal and substituted ammonium cyanides) as bases, and a number of neutralization reactions have been followed by means of conductimetric titrations. Indicators also give colour changes in this solvent. Solvolysis reactions have also been observed (*e.g.* $\text{Ag}_2\text{SO}_4 \rightarrow \text{AgCN}$; $\text{RCOCl} \rightarrow \text{RCOCN}$) and amphoteric behaviour is found in a few instances. For example, when triethylammonium cyanide is added to a solution of ferric chloride in hydrogen cyanide, ferric cyanide is first precipitated, but dissolves in excess of the base,



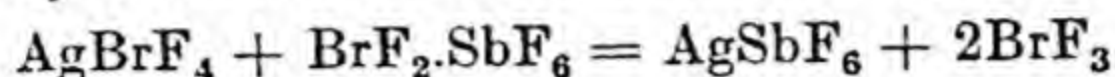
Bromine Trifluoride.—The great reactivity of bromine trifluoride (b.p. 127°) limits its use as a solvent to fluorides of metals and non-metals. In the pure state it has a specific conductivity at 25° of $8 \times 10^{-3} \text{ ohm}^{-1} \text{ cm.}^{-1}$, attributed to ionization into the BrF_2^+ cation and the BrF_4^- anion. Its reaction with fluorides leads to the formation of a number of new compounds analogous to acids and bases, all of which are more or less soluble and enhance the conductivity of the solvent. The following have been isolated.³²

³¹ Jander, *op. cit.*, p. 120. A comprehensive review of the field is given.

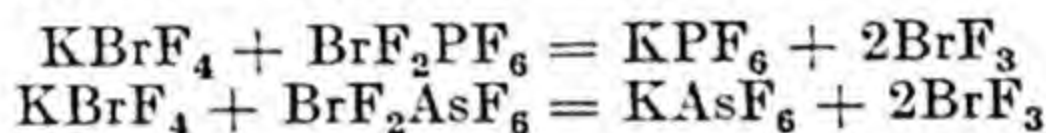
³² Sharpe and Emeléus, *J.C.S.*, 1948, 2135; Woolf and Emeléus, *J.C.S.*, 1949, 2865; 1950, 164, 1050; Sharpe, *J.C.S.*, 1949, 2901; Woolf, *J.C.S.*, 1950, 1053; Gutmann and Emeléus, *J.C.S.*, 1950, 1046.

Bases*Acids*

These compounds decompose thermally with liberation of bromine trifluoride. It is possible to follow the neutralization of an acid with a base by a conductimetric titration, *e.g.*



Reactions of this type have proved useful in the preparation of a range of complex fluorides, the applicability of the method being widened by the apparent existence in solution of a number of acids and bases which are too unstable to be isolated in the pure state. The pentafluorides of phosphorus and arsenic, for example, probably exist in bromine trifluoride solution as the acids BrF_2PF_6 and BrF_2AsF_6 , and if these solutions are allowed to react with potassium bromotetrafluoride the following reactions occur:



The nitronium and nitrosonium ions (NO_2^+ , NO^+) also appear to exist in bromine trifluoride solution as the bases NO_2BrF_4 and NOBrF_4 and, by reaction with acids, will give such compounds as NO_2BF_4 , NO_2AuF_4 , NO_2AsF_6 , NOBF_4 and NOPF_6 .³³

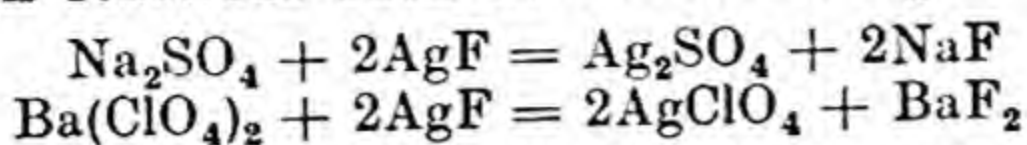
Anhydrous Hydrogen Fluoride.—Anhydrous hydrogen fluoride (b.p. 19.5°) is an associated liquid with a high dielectric constant, a low specific conductivity ($1.4 \times 10^{-5} \text{ ohm}^{-1} \text{ cm.}^{-1}$), and good solvent properties. The analogy between the chemistry of its solutions and those in water and ammonia is somewhat limited, but, largely as a result of the work of Fredenhagen and his collaborators,³⁴ a number of interesting points have emerged.

The fluorides of the alkali metals, ammonium, silver, thallium and, to a smaller extent, of magnesium and the alkaline earth metals dissolve in hydrogen fluoride and yield their simple ions. A few other salts (NaNO_3 , AgNO_3 , Na_2SO_4 , K_2SO_4 , and alkali chlorates, bromates, iodates, perchlorates and periodates) dissolve and form fairly stable conducting solutions, though the majority of inorganic substances are decomposed (metal chlorides give fluorides, for example, and hydrogen chloride, which is practically insoluble in hydrogen fluoride, escapes). The existence of ions

³³ Woolf, *J.C.S.*, 1950, 1053.

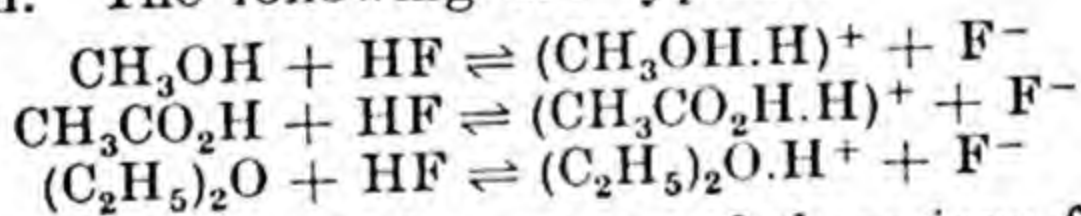
³⁴ For bibliography, see Jander, *op. cit.*, p. 6 *et seq.*

other than fluoride is shown by the occurrence in hydrogen fluoride of precipitation reactions such as the following:



It may be noted in passing that hydrogen fluoride forms a number of addition compounds with metallic fluorides (*e.g.* KF, HF ; $\text{KF}, 2\text{HF}$; $\text{KF}, 3\text{HF}$; $\text{NH}_4\text{F}, \text{HF}$). These might be thought to be analogous to compounds containing water of crystallization, which, in the solid state, contain water molecules as structural units. In these acid fluorides, however, the limited number of structural determinations available indicate the presence of the $(\text{HF}_2)^-$ anion. The anion is believed to exist in aqueous solutions of hydrogen fluoride in equilibrium with the simple fluoride anion. It is probable that the simple fluoride anion in anhydrous hydrogen fluoride is also associated to some extent with HF as $(\text{HF}_2)^-$. It is likely that the hydrogen ion is also associated with a solvent molecule as $(\text{H}_2\text{F})^+$.

A number of organic substances, including the hydrocarbons, are almost insoluble in hydrogen fluoride. A few, such as the alkyl fluorides, dissolve to give non-conducting solutions, but a great many others are either decomposed or polymerized. A further group, which includes alcohols, aldehydes, ketones, ethers, acids, acid anhydrides, certain nitrogen compounds and carbohydrates, give conducting solutions, the ions in which are a complex cation, containing the organic molecule associated with a proton, and the fluoride anion. The following are typical:



Fredenhagen has deduced the nature of these ions from measurements of molecular conductivity and the elevation of boiling-point. This interpretation of the cause of the conductivity is supported by the isolation of the compounds $(\text{C}_2\text{H}_5)_2\text{O} \cdot 2\text{HF}$, $\text{C}_2\text{H}_5\text{OH} \cdot \text{HF}$ and $\text{CH}_3\text{OH} \cdot \text{HF}$, which will probably be found to conduct electricity when in the pure state.

Miscellaneous Solvent Systems.³⁵—The general principles brought out in the foregoing pages are further supported by experimental work on a number of other systems, the ionization mechanisms for which are given on page 518.

In these systems the studies so far made do not provide so complete a picture as in the case of, say, ammonia. All of the compounds, however, can function as ionizing solvents. In nitric acid the metal nitrates function as bases and a few substances capable of

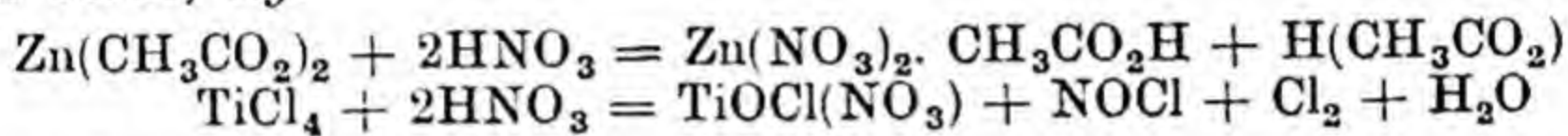
³⁵ See Jander, *op. cit.*

Substance	Sp. Cond. ohm ⁻¹ cm. ⁻¹	Ionization
HNO ₃	8.9×10^{-3}	$2\text{HNO}_3 \rightleftharpoons (\text{H.HNO}_3)^+ + \text{NO}_2^-$
I ₂	1.7×10^{-4} to 0.9×10^{-5}	$2\text{I}_2 \rightleftharpoons \text{I}^+ + \text{I}_3^-$
(CH ₃ CO) ₂ O	$2-5 \times 10^{-7}$ (25°)	$(\text{CH}_3\text{CO})_2\text{O} \rightleftharpoons (\text{CH}_3\text{CO})^+ + (\text{CH}_3\text{COO})^-$
SeOCl ₂	2×10^{-5} (25°)	$2\text{SeOCl}_2 \rightleftharpoons (\text{SeOCl.SeOCl}_2)^+ + \text{Cl}^-$
COCl ₂		$2\text{COCl}_2 \rightleftharpoons (\text{COCl.COCl}_2)^+ + \text{Cl}^-$

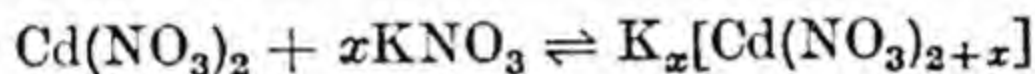
ionizing to give a proton (*e.g.* HClO₄) as acids. It is thus possible to carry out as a conductimetric titration the reaction between potassium nitrate and perchloric acid.



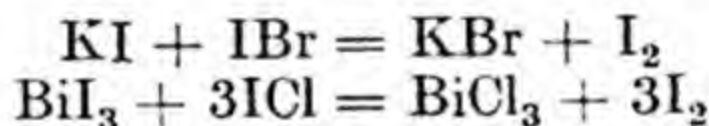
Sulphuric acid functions similarly as an acid. In addition, solvolysis can occur, *e.g.*



In a few instances amphoteric behaviour is observed, *e.g.*

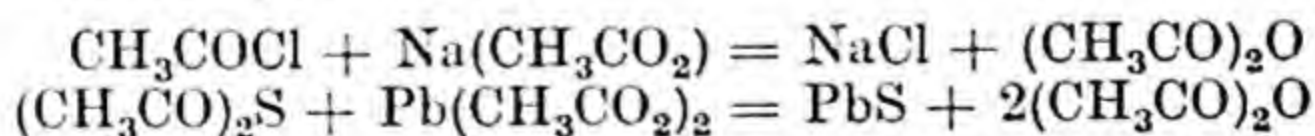


In liquid iodine, the iodides function as bases, while all the derivatives of 'positive' iodine function as acids. A number of neutralization reactions have been studied, *e.g.*



Amphoteric behaviour is found when iodides dissolved in liquid iodine react with excess of a 'base,' such as potassium iodide, forming complexes such as K₂(HgI₄) and K₃(BiI₆).

In acetic anhydride, acetyl derivatives function as acids and acetates as bases and neutralization reactions occur between these two types of compound, *e.g.*

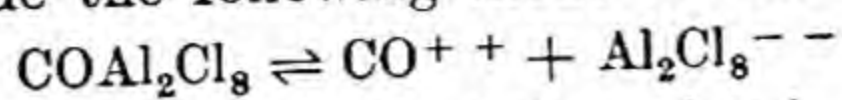


In selenium oxychloride a number of metallic chlorides are soluble and form conducting solutions (*e.g.* NaCl, NH₄Cl, FeCl₃).³⁶ Stannic chloride forms the compound SnCl₄.2SeOCl₂, which may be rewritten as a salt of the (SeOCl)⁺ cation, (SeOCl)₂SnCl₆. Carbonyl chloride resembles selenium oxychloride in its solvent properties. German³⁷

³⁶ *J. Amer. Chem. Soc.*, 1925, **47**, 2466; Smith, *Chem. Reviews*, 1938, **23**, 165.

³⁷ Germann and Gagos, *J. Phys. Chem.*, 1924, **28**, 965.

has postulated for the compound $\text{COCl}_2 \cdot 2\text{AlCl}_3$ formed with aluminium chloride the following mode of ionization :



(It is, however, more probable that the anion is AlCl_4^- .) Electrolysis of the solution gives carbon monoxide at the cathode and chlorine at the anode, and the solutions are able to dissolve metals with evolution of the same gas. Iodine trichloride, arsenic trichloride and the chlorides of antimony and sulphur also give conducting solutions : these clearly merit much closer study.

CHAPTER XVIII

RADIOACTIVITY AND ATOMIC DISINTEGRATION

Whilst the outer electronic structure of the atom is susceptible to experimental investigation by the methods of physics and chemistry, our knowledge of the central nucleus is derived largely from the study of radioactivity. All the elements from bismuth to uranium, and a few of the lighter elements, have naturally radioactive isotopes. In addition, radioactive isotopes of all the lighter elements and of a number of elements beyond uranium, the so-called transuranic elements, may be made artificially.

The phenomenon of radioactivity entails the spontaneous disintegration of the nucleus at a rate which is a characteristic for each particular active isotope. In the early development of the subject, when only naturally occurring radioactive elements were studied, three types of rays, α -, β - and γ -rays, were recognized. Of these, α -rays consist of helium nuclei with a double positive charge and with a characteristic initial velocity, varying from case to case, but of the order of 10^9 cm./sec. In any medium the particles have a definite range and are able to produce intense ionization in their paths. The β -rays are negative electrons which are also emitted with a high velocity, though, in general, particles from one and the same source show a wider range of energies. These particles lose their energy less readily in passing through matter, and consequently they cause much less ionization in their tracks and have larger ranges than α -particles of comparable initial energies. The γ -rays consist of electromagnetic radiation of frequency higher than that of X-rays.

The characterization of these three types of radiation depends, in the case of α - and β -rays, on the direct determination of the ratio of mass to charge for the particles by measurements of their deflection in a magnetic field, on the direct measurement of the charge carried by a given number of particles and, in the case of α -rays, on the spectroscopic proof that α -rays which have lost their energy (and acquired the necessary orbital electrons in the process) are identical with helium. Since the discovery of artificial radioactivity (*vide infra*) two further fundamental particles have been recognized as products of nuclear disintegration. The first of these,

the positive electron, is identical with the negative electron but of opposite charge. The second, the neutron, has a mass almost identical with that of the proton, but is uncharged. The proton, which is the nucleus of the hydrogen atom, and the corresponding particle from deuterium, the deuteron, are also produced in nuclear disintegrations of certain types.

The Disintegration Theory.—In the spontaneous nuclear disintegration of all radioactive isotopes the number of atoms undergoing disruption in unit time is a constant fraction, λ , of the number of atoms, N , present at that time. This applies if N is very large. If it is not, λ is best defined as the probability of disintegration of any one atom. It follows that the number of atoms of the unstable radio element remaining decreases exponentially with time according to the equation $N = N_0 e^{-\lambda t}$, where N_0 is the number of atoms originally present. The quantity λ is known as the *disintegration constant* and is a characteristic of each radioactive isotope. The quantity $\frac{1}{\lambda}$ has the dimensions of time and represents the *statistical mean life* of the atoms of the unstable element. Of more direct utility is the *half-value period* or *half-life*, T , the time in which the activity decays to one half of its initial value. It follows from the exponential nature of the decay that $T = 0.69/\lambda$.

The half-value periods of radioactive isotopes vary enormously. For a number of elements, among which uranium and thorium may be mentioned, the activity is sensibly constant, showing that the half-value periods are very long. The products of their decay are not, however, stable elements, but are themselves radio elements which, in the instances cited, are short-lived. These short-lived products yield yet other radioactive products and this process continues until the stable end product of the decay series is reached. In any such decay series an equilibrium condition will be set up in which each element is being formed at the same rate as that of its decay. If the decay constants of the members of the series present $\lambda_1, \lambda_2, \lambda_3$, the numbers of atoms of each member of the series present at equilibrium (N_1, N_2, N_3, \dots) will be given by the relationship

$$\lambda_1 N_1 = \lambda_2 N_2 = \lambda_3 N_3 = \dots$$

The Determination of Half-Value Periods.—The half-value periods of radioactive isotopes vary so widely that no single experimental method is applicable to the determination of all. Long periods may be determined by counting the number of particles emitted from a known weight of the isotope in a given time. This gives directly the fraction of the total number of atoms present which decay. Alternatively, long periods may be determined by

using the principle of radioactive equilibrium. For example, in minerals of great geological age, equilibrium must be established between uranium and radium. The ratio of Ra : U in the uranium minerals is, in fact, uniformly $3.3 \times 10^{-7} : 1$ by weight. The decay constant of radium, as determined by the direct counting of α -particles, is 1.39×10^{-11} per sec., so that by the principle of radioactive equilibrium we have

$$\lambda_U = 3.3 \times 10^{-7} \times 1.39 \times 10^{-11} \times \frac{238}{226},$$

whence $T_{1/2} = 4.51 \times 10^9$ years.

For moderately long half-lives counts may be made of the rates of emission of particles at two suitably separated times. The approximate lower limit of this method is a half-life of 20 minutes. The upper limit is 1000–2000 years. For half-lives somewhat shorter than 20 minutes it is also possible to count the activity at two different times, but a correction must be made for the decay of the sample during the time of counting.

Very short half-lives may, in the case of the natural radioactive isotopes, be determined by applying the empirical Geiger-Nuttall relationship between the velocity (or range) of an α -particle and the disintegration constant of the process by which it is ejected. A plot of the logarithm of the α -particle range against the logarithm of the decay constant is a straight line for each of the four disintegration series. If then the range of an α -particle from a short-lived source is measured, the disintegration constant may be obtained from the Geiger-Nuttall plot for the appropriate decay series. A like relationship may be applied, though with more difficulty on account of the velocity distribution, to β -decay processes.

For short-lived isotopes of artificial origin (*vide infra*) a mechanical arrangement is sometimes used. If, for example, a target material is rendered radioactive by bombardment with some type of particle, it may be mounted on a rotating circular disc. Irradiation and counting take place at opposite ends of a fixed diameter and the speed of rotation is varied until a maximum counting rate is observed. The statistical mean life $\left(= \frac{1}{\lambda} \right)$ is then equal to the

time of revolution of the disc. Determinations of extremely short half-lives for artificial radio elements have also been measured by adapting the cathode ray oscillograph to measure the time interval between the interruption of irradiation and the occurrence of the decay. Apart from short-lived isotopes, artificial radio elements may be studied by the same methods as natural radio elements.

In studying radioactive substances, mixtures are very commonly

encountered. There may be mixtures in the sense that several types of radiation are emitted simultaneously, or there may be different species present emitting the same type of radiation with different half-lives. In these circumstances the use of screens may enable some of the radiation to be absorbed, thus rendering possible the counting of a single component. Alternatively, it is possible to measure a composite decay curve, plotting the logarithm of the activity against time, when the various decay processes appear as straight lines joined by curves of varying slope. The slopes of the linear sections give the decay constants directly. A typical curve of this sort is shown below.

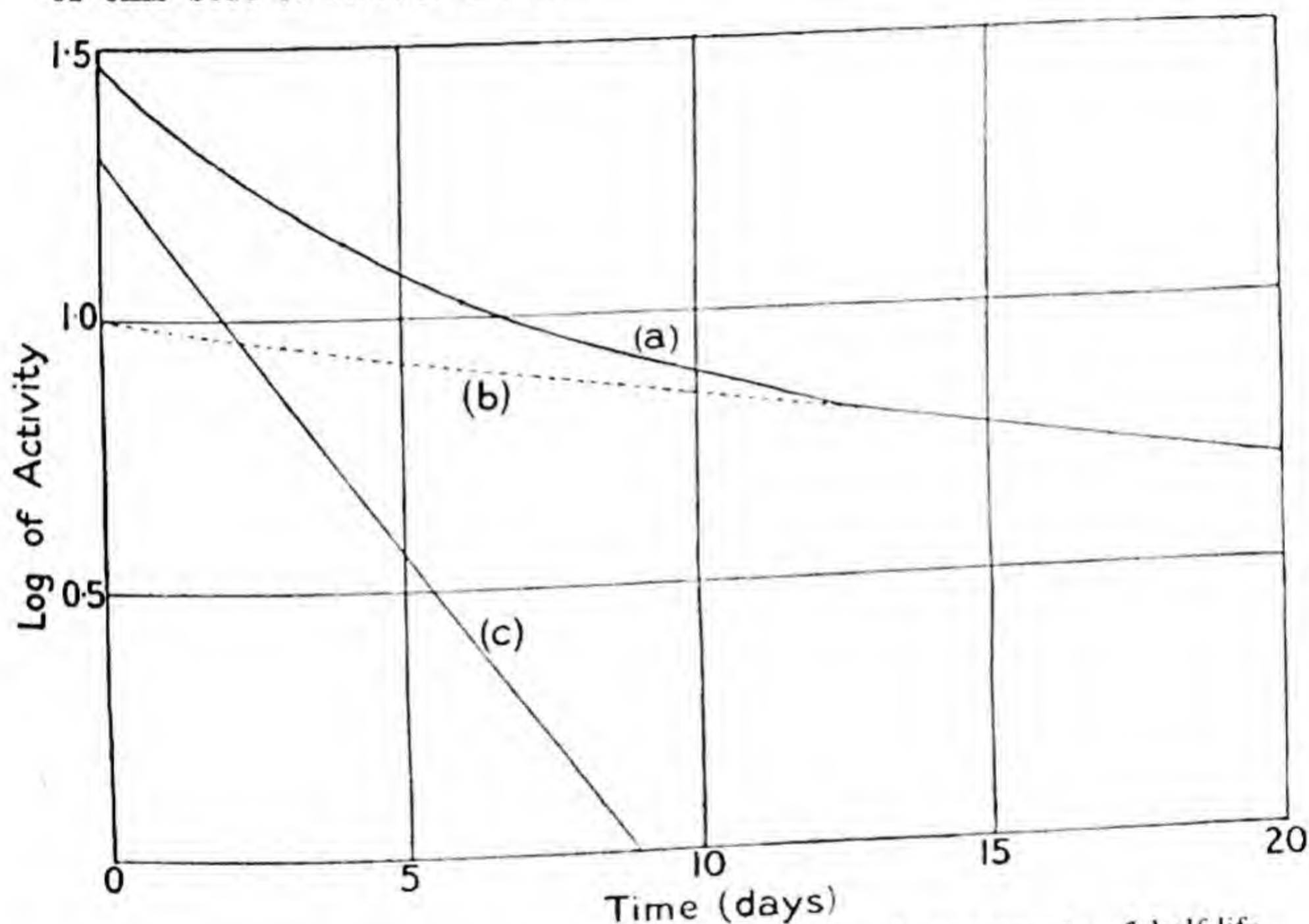


FIG. 67.—(a) Composite decay curve for a mixture of components of half-life 20 and 2 days. (b) Decay of long-lived element. (c) Decay of short-lived component.

The Radioactive Displacement Law.—Early in the development of the subject it was realized that there was a connexion between the radiation emitted and the chemical relationship between the parent undergoing radioactive decay and the daughter element. This is summarized as follows:

- (a) When an α -particle is emitted the atomic weight is decreased by four units and the nuclear charge by two units. The

decay product is thus displaced two groups to the left in the periodic table.

- (b) When a β -particle is emitted the loss of one negative charge from the nucleus is equivalent to a gain of one positive charge, and the decay product will therefore belong to the next group to the right in the periodic table. There is no significant change in atomic weight.

In addition it should be noted that positron emissions will give a product belonging to the next group to the left and with an atomic number one unit less, whilst gain or loss of a neutron changes only the atomic weight, *i.e.* the product is isotopic with the parent. These considerations played an important part in the formulation of the three decay series of classical radioactivity, but, since the form of these has been changed so much by the discovery of the transuranic elements, a discussion of the decay series will be deferred until later in this Chapter (*see p. 536*).

Nuclear Disintegration and Artificial Radioactivity

Nuclear Disintegration by α -Particles.—The first indication that what was believed to be a stable atomic nucleus could be disrupted was afforded by Rutherford's observation, in 1919, that fast α -particles from Ra-C give rise in nitrogen to a small number of particles with ranges up to 40 cm. in air. The magnetic deflection of these particles showed them to be protons which could only have originated in the nitrogen nucleus.



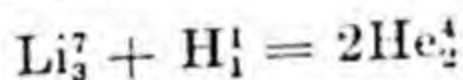
Similar disintegrations were observed by Rutherford and Chadwick for all the elements between boron and potassium with the exception of carbon and oxygen.¹ The process was first photographed by Blackett² with the aid of the Wilson cloud chamber. He found that in the rare disintegrating collisions the α -particle disappeared, giving rise to two new tracks. One of these, that of the proton, was long, whilst the heavier product of the nuclear reaction gave only a short spur. In present-day nomenclature this is referred to as an (α, p) reaction. In the range of elements mentioned and with the energies available in natural α -particles it occurs very seldom—roughly twenty times for each million α -particles passing through the medium. The positive charge on the nucleus tends to repel the approaching α -particle and as a result the change becomes less probable in the heavier elements of greater nuclear charge.

¹ *Phil. Mag.*, 1921, **42**, 809; 1922, **44**, 417.

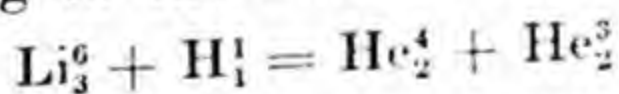
² *Proc. Roy. Soc.*, 1925, **A**, 107, 349.

To some extent this limitation may be offset by accelerating helium ions to energies greater than those of natural α -particles by means of the cyclotron or some other device for producing fast particles.³ The limit of energies in natural α -particles is of the order of 2–8 million electron volts (Mev.),⁴ whereas 'artificial' α -particles with energies up to > 300 Mev. have been obtained. With high energy α -particles from the cyclotron reactions in heavier nuclei may be brought about (e.g. $\text{As}^{75}(\alpha, n)\text{Br}^{78}$; $\text{Bi}^{209}(\alpha, 2n)\text{At}^{211}$; $\text{Zn}^{64}(\alpha, p)\text{Ga}^{67}$).

Nuclear Disintegration by Protons and Deuterons.—By reason of its smaller charge, it is to be expected that the proton should be capable of surmounting the potential barrier around a nucleus at lower energies than an α -particle. That this is indeed the case was first shown by Cockroft and Walton in 1932.⁵ Protons were accelerated to energies of 125,000 electron volts and used to bombard lithium salts. Massive particles were emitted from the target, their nature being convincingly shown by Wilson cloud chamber photographs, which revealed two equivalent particle tracks corresponding to the reaction:



That the isotope Li^7 was concerned in this reaction was shown by bombarding lithium isotopes separated in small amounts by means of the mass spectrograph.⁶ In the bombardment of the isotope Li^6 two dissimilar particles, each with a nuclear charge of $+2$, were formed, corresponding to the nuclear reaction:



These and other early experiments on nuclear disintegration by high velocity particles were followed by a period of intensive exploration of the new field and other types of reaction were discovered. The chief of these are summarized, with examples, in the table on p. 526.

It will be noted that the majority of these reactions involve the bombardment of light nuclei. A further point, the formation of unstable products in nuclear reactions, is discussed in detail later. The production of neutrons (e.g. in (α, n) reactions) has been of great

³ For a description of the cyclotron, etc., see Friedlander and Kennedy, *Introduction to Radiochemistry* (John Wiley and Sons, Inc., New York, 1949).

⁴ An electron volt is the energy needed to raise an electron through a potential of one volt. The million electron volt unit (Mev.) is in common use.

⁵ *Proc. Roy. Soc.*, 1932, A, 137, 229; 1934, 144, 704; 1935, 148, 225; 1936, 154, 246, 261; see also Lawrence, *Phys. Rev.*, 1932, 40, 19; 1934, 45, 346, 428, 608.

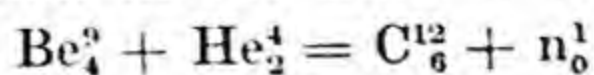
⁶ Oliphant, Shire and Crowther, *Proc. Roy. Soc.*, 1934, A, 146, 922.

Table 1

Type of Reaction	Example	Typical Nuclei giving Stable Products	Typical Nuclei giving Unstable Products
(α ,p)	$F_9^{19} + He_2^4 = Ne_{10}^{22} + H_1^1$	$B^{10}, N^{14}, F^{19}, Na^{23}, Mg^{24}, Al^{27}, Si^{28}$	$Li^7, Mg^{25}, Mg^{26}, Ca^{40}$
(α ,n)	$Na_{11}^{23} + He_2^4 = Al_{13}^{26} + n_0^1$	Li^7, Be^9, Al^{26}	$Li^6, B^{10}, N^{14}, F^{19}, Mg^{26}, Al^{27}, P^{31}, K^{39}$
(p, α)	$N_7^{14} + H_1^1 = C_6^{11} + He_2^4$	$Li^6, Li^7, Be^9, F^{19}, N^{14}, Na^{23}, Mg^{26}$	
(p, γ)	$C_6^{12} + H_1^1 = N_7^{13} + \gamma$	Be^9, F^{19}	C^{13}
(d, α)	$C_6^{12} + H_1^2 = B_5^{10} + He_2^4$	$Li^6, Be^9, B^{11}, C^{12}, N^{14}, F^{19}, Na^{23}, Al^{27}$	Mg^{24}
(d,n)	$Be_4^9 + H_1^2 = B_5^{10} + n_0^1 + \gamma$	$H^2, Be^9, B^{11}, Na^{23}, Al^{27}$	B^{10}, N^{14}
(d,p)	$B_5^{10} + H_1^2 = B_5^{11} + H_1^1$	B^{10}, C^{12}, N^{14}	$Li^7, Be^9, B^{11}, Na^{23}, Al^{27}, H^2$

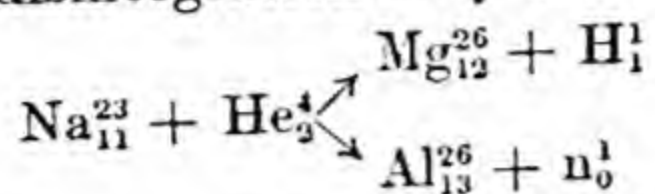
importance in many recent developments, and is dealt with in the following section.

The Neutron.—The bombardment of beryllium with α -rays from polonium was observed by Chadwick⁷ to give a radiation of great penetrating power, which produced no ionization along its path but was able to eject protons from hydrogen, lithium, carbon and other elements. From a consideration of the conservation of energy and momentum in these processes, it was shown that the phenomena were not consistent with the hypothesis that a true radiation was involved, but required the postulation of a new kind of particle with unit mass and zero charge—the neutron. The neutron is produced from beryllium in the nuclear reaction

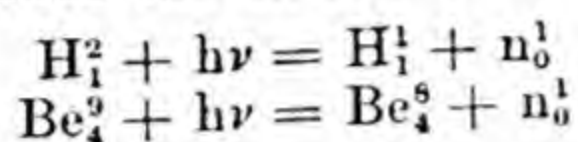


⁷ *Proc. Roy. Soc.*, 1932, A, 136, 692; 1933, 142, 1.

By balancing the masses and energies of the various particles it may be deduced that the neutron formed has a maximum kinetic energy of 7.8 Mev., corresponding with a velocity of 3.9×10^9 cm. per sec. The yield in this case is about thirty neutrons per million α -particles. Lithium, boron, fluorine, sodium, magnesium, aluminium and phosphorus also give rise to neutrons. In the case of several elements the disintegration may follow two courses, *e.g.*

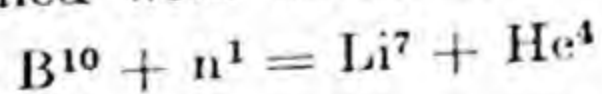


A second mode of liberation of neutrons is by a species of nuclear photoelectric effect⁸ from the nuclei of deuterium and beryllium



The first reaction is produced by γ -rays from ThC'' (E_{max} 2.62 Mev.) but not by those from actinium decay products (E_{max} 0.8 Mev.). An energy balance for the reaction enables the mass of the neutron to be deduced with some accuracy. The proton formed carries away about 0.25 Mev. of kinetic energy and the neutron, having almost the same mass, will account for an equal amount. About 2.12 Mev. are therefore expended in the disintegration process, equivalent to 0.0022 atomic weight units of mass. Taking for deuterium and hydrogen the masses 2.0144 and 1.0082 respectively, it follows that the mass of the neutron is 1.0084.

Neutrons are formed in the bombardment of a number of elements with fast protons and deuterons, and also in nuclear fission. Examples of these processes are given later. Since the neutron produces no ions in its path it must be detected by secondary effects which it produces, *e.g.* by detecting and measuring the α -particles emitted in the following reaction, which occurs when neutrons enter an ionization chamber filled with boron trifluoride.



Neutron fluxes are determined by measuring the radioactivity induced in a suitable metal foil (*e.g.* of indium or gold) in a given time. This is proportional to the neutron flux and, knowing the neutron capture cross-section of the foil material, will give a value for the neutrons impinging on unit area of the metal.

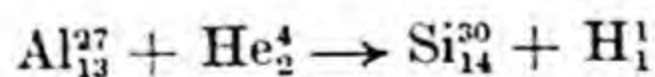
Artificial Radioactivity: α -Particle Bombardment.—In 1934 a new phenomenon of fundamental importance was discovered by Mme I. Curie and M. Joliot,⁹ namely, that metastable isotopes

⁸ Chadwick and Goldhaber, *Proc. Roy. Soc.*, 1935, A, 151, 479.

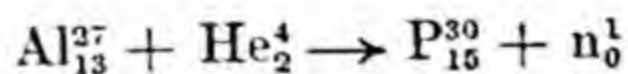
⁹ *Compt. rend.*, 1934, 198, 254, 559, 2089; *J. Chim. Physique*, 1934, 31, 611.

of light elements may in some cases be formed as a result of bombardment with α -particles, and that these metastable nuclei decay in a manner exactly analogous to the decay of the heavy radioactive elements. It was observed that, by the bombardment of boron and aluminium by α -particles, positive electrons were emitted in addition to protons and neutrons. The positive electron, or *positron*, a particle with the same mass as an electron, but with a unit positive charge, had been first detected in 1932, being formed, together with a negative electron, by the action of the penetrating cosmic radiation. Penetrating γ -radiation may also give rise to positrons on absorption in matter, one quantum of γ -radiation or cosmic radiation being apparently converted into a positive-negative electron pair. The energy required for the process, calculated from the mass of the two electrons, is about 1.02 million e.v. It appears that the positron, unlike the negative electron, is essentially short-lived. When the energy of a positron has fallen to a low value, it may be annihilated on encounter with an electron, two quanta of radiation being liberated.

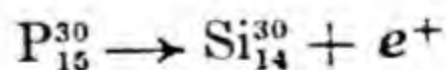
In these experiments the emission of positrons increased during irradiation to a limiting value. After removing the source of α -particles, the emission of protons and neutrons ceased, but the emission of positrons continued, decreasing exponentially with time. The process had, therefore, all the characteristics of the formation and decay of a short-lived radioelement. Since the transmutation immediately effected by the α -particles may result in the ejection either of a proton, or of a neutron, it is clear that in the latter case a metastable species must result, which subsequently loses a positron. The final product is then identical with that obtained directly by the $(\alpha;p)$ process. Thus, in the case of aluminium, the alternatives are



or



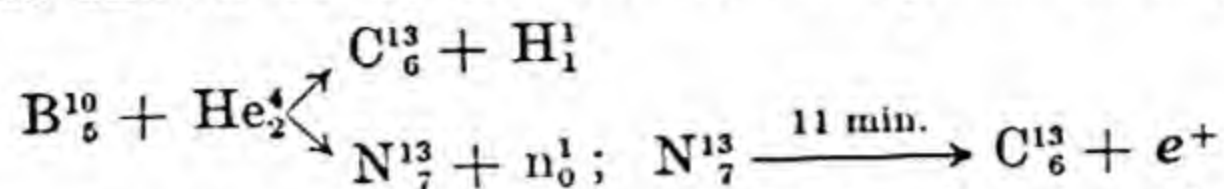
followed by



In the case cited, about 5 per cent of the total disintegration proceeds by the second process; the radioactive phosphorus isotope has a half-value period of 3.2 minutes.

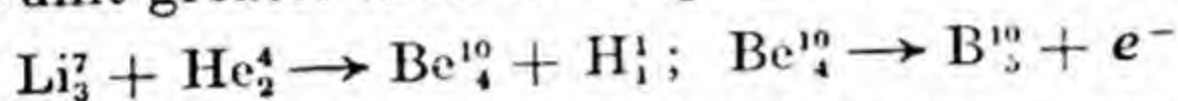
The radioactivity was proved chemically to be due to an isotope of phosphorus. On dissolution of the irradiated aluminium foil in hydrochloric acid, the radioactivity was carried by the hydrogen evolved, presumably in the form of phosphine; if the foil was dissolved in a mixture of hydrochloric and nitric acids, and sodium

phosphate was added as a carrier, the addition of a zirconium salt carried the radioactivity quantitatively down with the zirconium phosphate precipitate. In a similar way, the radioactivity induced in boron was shown to be due to an isotope of nitrogen:

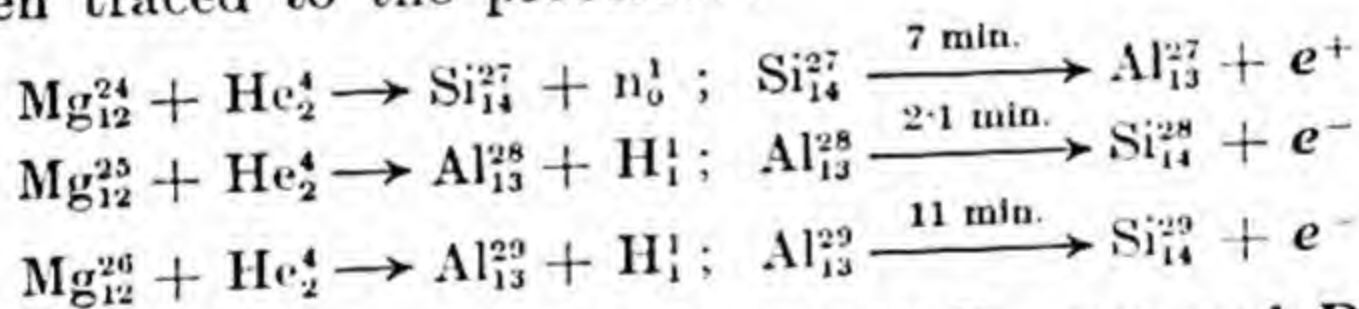


When boron nitride was irradiated, and subsequently dissolved rapidly in hot caustic alkali, all the positron activity was carried over with the ammonia generated. The formation of short-lived radioelements in (α ;n) transformations has since been detected with other elements (see p. 526).

Radioactive isotopes may also be formed as the products of (α ;p) reactions, whereby a species is produced having an atomic number one unit greater than the original element. Thus, with Li_3^7 ,



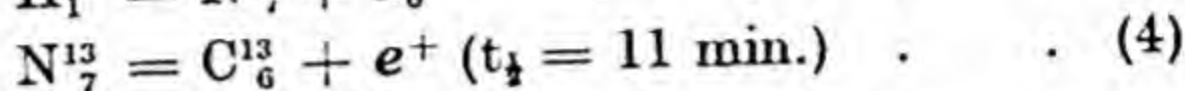
Metastable nuclear species formed in this way revert to stable species by a β -ray transformation. Since each isotope of a mixed element reacts independently on bombardment, such elements may display complex effects, positive and negative electrons being emitted at different decay rates. Magnesium, for example, displays after irradiation two β -activities and one positron activity, which have been traced to the processes:



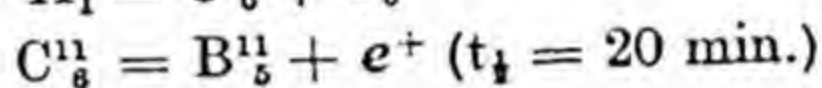
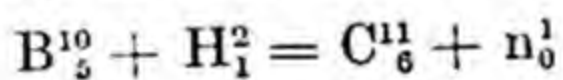
Artificial Radioactivity produced by Proton and Deuteron Bombardment.—Following the work of Curie and Joliot upon the formation of radioelements in α -particle transformations, it was found that other types of nuclear reaction could give rise to metastable species. Examples of such transformations produced by high-speed protons and deuterons are included in Table 1. These reactions call for little comment. The instability which manifests itself in the phenomenon of artificial radioactivity is a characteristic of the particular nucleus in question. The same unstable nucleus, produced in different ways, will show the same decay characteristics. Normally the decay in the case of an artificially produced species is a single process, but there are instances of alternative decay mechanisms for one and the same nucleus, just as in the natural radioactive decay series.

The methods of characterizing chemically the species responsible

for the observed radioactivity are often extremely interesting and may be illustrated by a few examples. Firstly we may consider the reaction produced on bombarding carbon with protons, which is represented by the equation (1) below



The same isotope is formed in either of the reactions (2) and (3) and decays according to reaction (4). As produced in reaction (3), the radioactive nitrogen was characterized by scraping off the surface layers of the carbon target, burning this product in a helium-air mixture, absorbing carbon dioxide and oxygen chemically and then passing the residual gas over calcium. The calcium nitride formed displayed the 11 min. positron activity, which was transferred to the ammonia formed by treating the nitride with water. In a similar manner the bombardment of boron with deuterons gives radiocarbon by a (d,n) transformation:



Here it was shown that if all gases were driven off from the boron trioxide target by heating, and mixed with carbon dioxide, then the radioactive species present accompanied the carbon dioxide on absorption in caustic potash. The absorption of radioactive material was not complete, however, since some of the radiocarbon driven off from the target material was present as carbon monoxide, which was recovered by adding inactive carbon monoxide to act as a carrier, oxidizing with hot copper oxide and absorbing in alkali. Many similar instances of chemical identification occur both in the earlier literature of this subject and in more recent work on the characterization of fission products (*vide infra*).

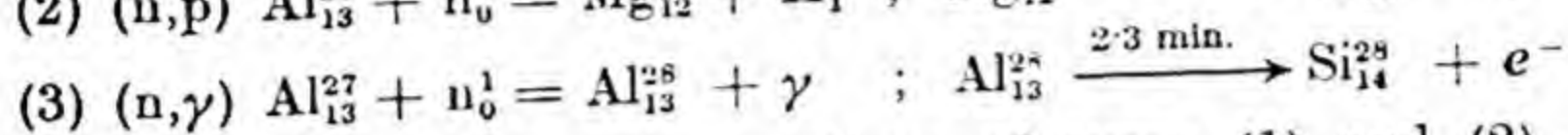
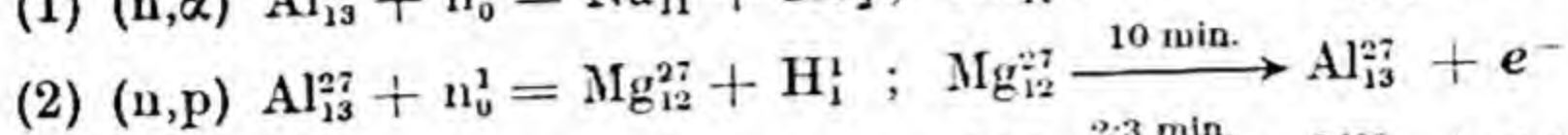
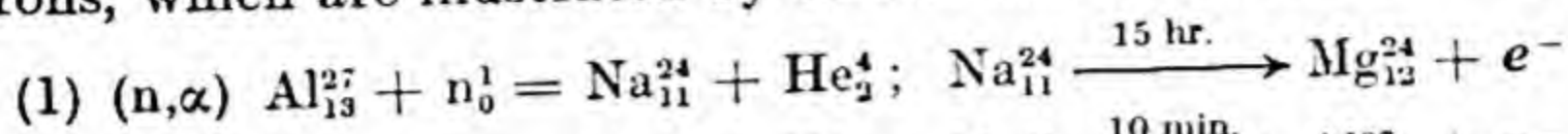
Irradiation with Neutrons.—It has already been pointed out that the powerful repulsive forces between atomic nuclei and positively charged particles tend to limit the disintegrating effects of α -particles, protons and deuterons to the lighter elements. The neutron, whilst it may have a very high energy, is exempt from these repulsions since it is uncharged. It is, accordingly, capable of penetrating and effecting transmutations in the nuclei of even the heaviest elements.

Following the discovery of the neutron, it was found by the Wilson cloud-chamber method that various nuclei were disintegrated by

collision with neutrons, an α -particle being ejected. Nitrogen, for example, undergoes an (n, α) reaction:

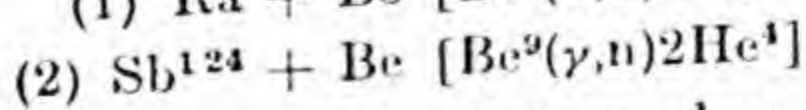
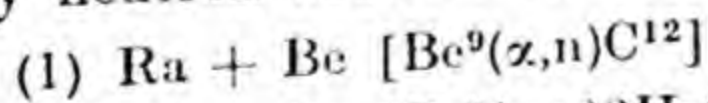


Fermi found three main types of nuclear reactions produced by neutrons, which are illustrated by results obtained with aluminium.



For neutrons of high energy reactions of types (1) and (2) are favoured, whereas capture reactions of type (3) occur more readily with low neutron energies. Fermi and his co-workers made the important discovery that neutrons may be slowed down to thermal velocities by passage through certain media (*e.g.* water, paraffin wax, pure graphite) in which the probability of occurrence of a nuclear reaction is particularly small. In such media the fast neutron loses energy by elastic collisions. The slow neutrons are captured readily by the majority of atomic nuclei, forming a nucleus isotopic with the capturing atom, but with a mass one unit greater (reaction of type (3)). Even with the heavy atoms, which can capture fast neutrons, the probability of the (n, γ) reaction is considerably greater with slow neutrons. The capture of slow neutrons presents a number of theoretical problems. The apparent collision area of the nucleus varies greatly from one element to another. Moreover in some cases there is preferential absorption of slow neutrons, the energy of which lies within a certain specific range—the so-called resonance energy.

Of sixty elements subjected by Fermi¹⁰ to neutron bombardment, forty gave rise to radioactive products, all of which were β -active. Since these early experiments the subject has been widely studied. The usual laboratory neutron sources are:



Neutron irradiations, either with fast or slow neutrons, are very readily made in a nuclear reactor in which high neutron fluxes are available (*vide infra*).

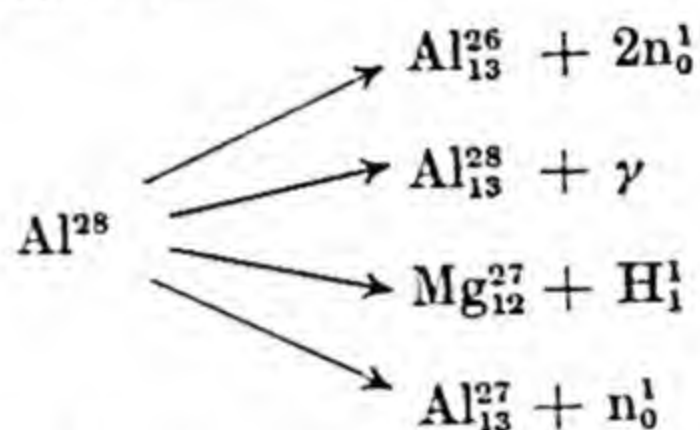
The Bohr Theory of Nuclear Reactions

The nucleus of an atom is believed to be a composite system containing protons and neutrons, and to have a complex structure

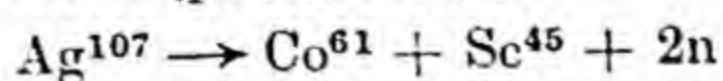
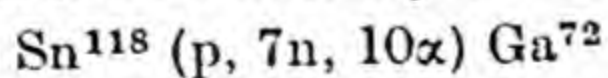
¹⁰ *Proc. Roy. Soc.*, 1934, A, 146, 483; 1935, 149, 522.

as regards energy relationships, roughly analogous to that associated with the extra-nuclear electrons. Most isotopes occurring in nature have stable nuclei, but for a few—those which are radioactive—there is a definite probability that the internal energy distribution will pass into an unstable phase, leading to the phenomenon of radioactive decomposition. That a similar instability can be induced by bombardment is not surprising. The incident particle hitting the nucleus is considered by Bohr to impart energy to the nucleus and to form a compound nucleus with a lifetime of $10^{-12} - 10^{-14}$ sec. During this time the extra energy becomes distributed and the nucleus becomes 'excited'.

It is inherent in the Bohr theory that the excited nucleus can disintegrate in several ways, and this is often found to be the case. When, for example, aluminium is bombarded with fast neutrons the initial change is $\text{Al}^{27} \rightarrow \text{Al}^{28}$, and the excited Al^{28} nucleus can dissociate as shown below:—



A great deal of progress has been made in the direction of predicting the relative probabilities of these competing nuclear reactions, which depend primarily on the energy of excitation. With high excitation energies more complex decomposition reactions, involving the emission of two or more particles, are observed (e.g. $(\alpha, 2n)$, (α, n, p) , $(\alpha, 3n)$). With very high energy bombarding particles generated in the cyclotron, reactions of much greater complexity occur, leading to large changes in the nuclear mass. This phenomenon, which has been termed spallation, may be illustrated by the following examples, taken from recent work by Seaborg and his collaborators.¹¹

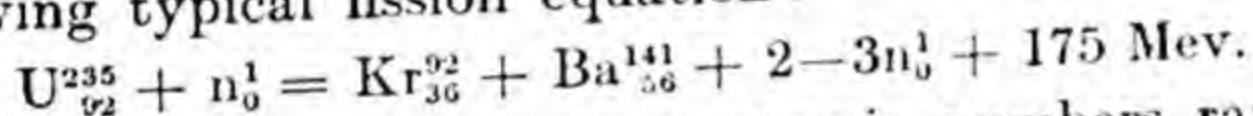


The first reaction is produced by protons of very high energy (> 230 Mev.) and yields seven neutrons and ten α -particles. In the second, which is induced by protons of moderate energy, the phenomenon is very much the same as fission. These studies are indeed rapidly opening up an entirely new chapter in the study of nuclear reactions.

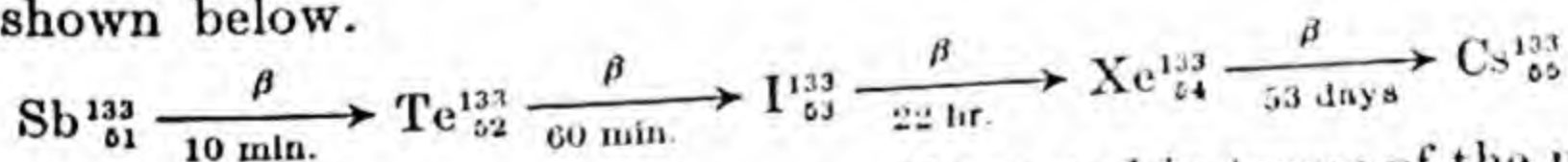
¹¹ Batzel and Seaborg, *Phys. Rev.*, 1950, **79**, 528.

Neutron Irradiation of Uranium.—The fact that neutron capture by a nucleus, followed by β -decay, leads to an element of atomic number one unit greater than that of the parent led Fermi and his associates to examine uranium in the expectation that an element of atomic number 93 could be synthesized in this way. The first experiments revealed four different β -activities in a uranium sample after slow neutron bombardment, which were attributed to new transuranic elements. Further work showed the number of activities to be even greater and, after a short period of confusion in the interpretation of these results, it was realized, largely as a result of the work of Hahn, that an entirely new phenomenon—nuclear fission—was involved.

Natural uranium contains three isotopes, U^{234} (0.006 per cent), U^{235} (0.7 per cent) and U^{238} (99.3 per cent). The first of these is present in such small amounts that it plays no important part in what follows. The second isotope, U^{235} , undergoes fission, while U^{238} is able to capture slow neutrons and build up transuranic elements. In the process of fission two lighter atomic nuclei are formed, together with fast neutrons. This process is illustrated by the following typical fission equation:



The nuclei formed in fission have atomic numbers ranging from 30 (Zn) to 63 (Eu) and atomic masses between 72 and 162. The fission products are themselves unstable nuclei, in which there is in general an excess of mass to charge over the value requisite for nuclear stability. This leads to the emission of β -particles from the initial product, a process which increases the nuclear charge without change of mass. A typical fission chain, in which an antimony isotope decays in four steps to a stable caesium isotope, is shown below.



The yield of fission products is generally stated in terms of the mass number. The yield curve for the fission of U^{235} is shown on p. 534. It has two well-defined maxima at masses of 95 and 139, and the most abundant fission products lie in these two regions. There are a number of isotopes formed in fission which have been produced from the cyclotron bombardment of suitable target materials. This is of great assistance in identifying the species present. Many species have, however, been separated and identified by the ordinary methods of analytical chemistry. Isotopes of krypton and xenon, for example, are both present and may be separated because of their chemical inertness and identified with the mass spectrograph. The

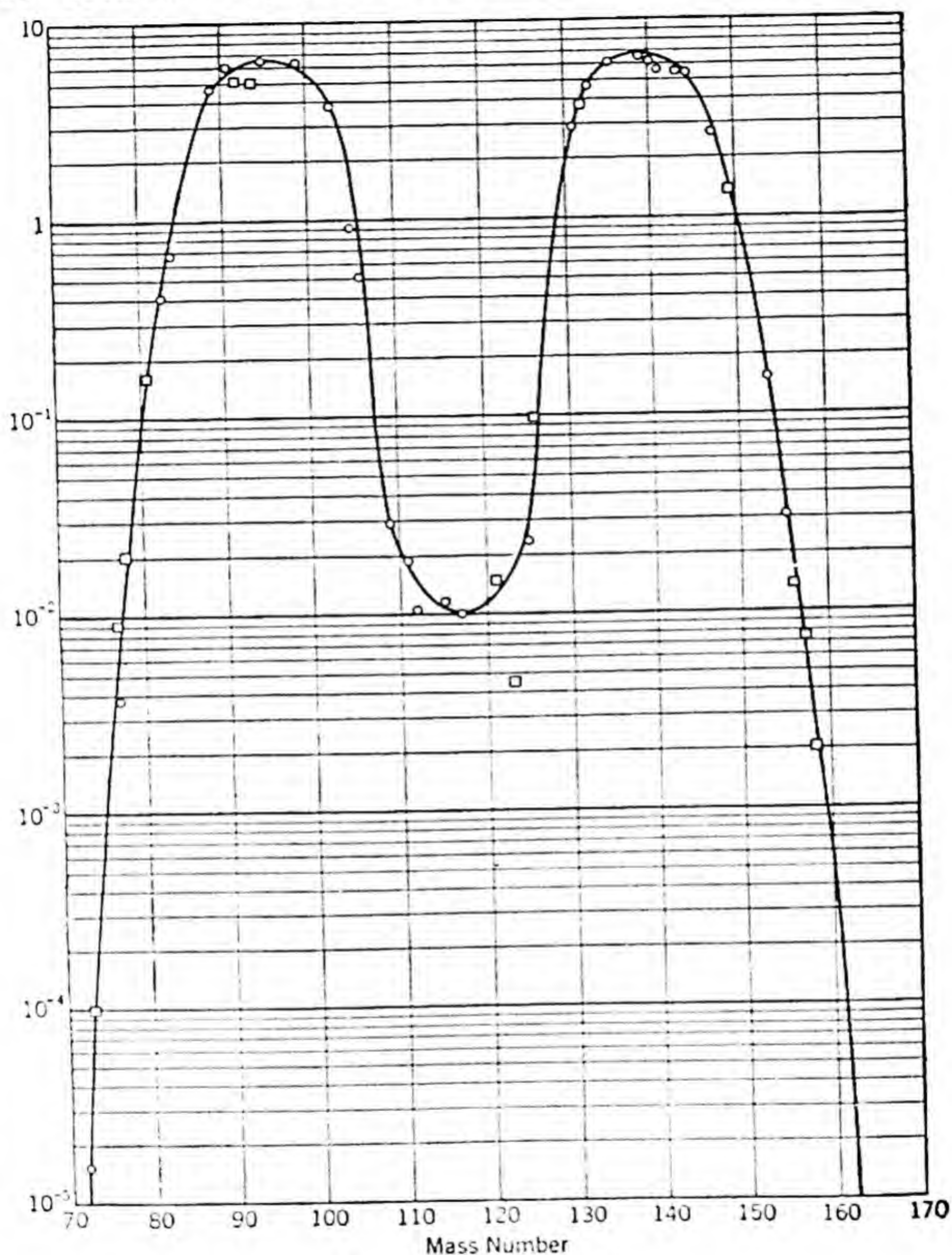


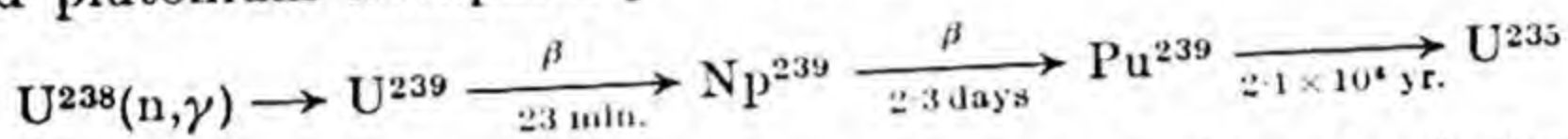
FIG. 68.—Fission yield %.

halogens bromine and iodine may be extracted from the mixed fission products by means of solvents, barium and strontium may be precipitated as sulphates, silver as its chloride and a large group of elements (Mo, Ru, Rh, Pd, Cd, In and Sn) as sulphides. Again, other elements (As, Sb, Sn, Se, Ge) may be volatilized as halides.

The quantities handled in these separations are usually very small and in order to facilitate manipulation it is best to add a few milligrams of an inactive compound of the element sought before undertaking a separation. Two isotopes formed in fission, namely the technetium isotope Tc_{43}^{99} with a half-life of 9.4×10^5 years, and the promethium isotope Pm_{61}^{147} with a half-life of 3.7 years, are formed in yields of 6.2 and 2.6 per cent, respectively, and are a valuable source of material for investigating the chemistry of these little-known elements (see pp. 390, 387).

Isotopes of other elements also undergo fission. Among these are Pu^{239} and U^{233} which are fissionable under slow neutron bombardment, and U^{238} and Th^{232} for which fast neutrons are effective.

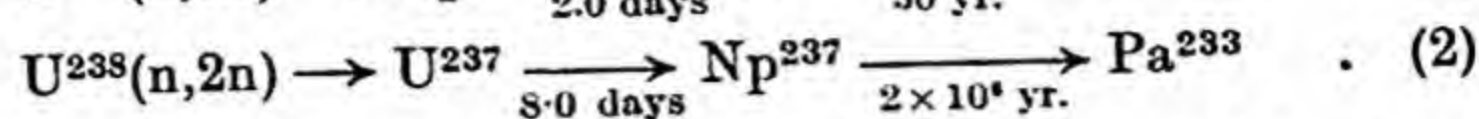
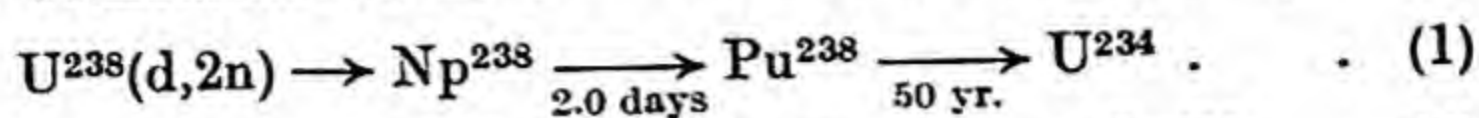
The Transuranic Elements.—The second process which occurs in the bombardment of natural uranium with slow neutrons is one of neutron capture followed by β -decay, leading to the neptunium and plutonium isotopes Np^{239} and Pu^{239} :



This process can occur with the neutrons formed in the fission of U^{235} , provided they are slowed down to suitable velocities for capture by U^{238} . This condition is established in the so-called atomic pile, which consists of a series of rods of pure uranium placed in a series of channels passing through a large mass of pure graphite or deuterium oxide, either of which has the property of slowing down neutrons without appreciable capture. There is a small amount of spontaneous fission in U^{238} , and the fast neutrons so produced, after being slowed in the surrounding medium, either cause fission of U^{235} , which produces more neutrons, or react with U^{238} to form neptunium and plutonium. Under suitable conditions a nuclear chain reaction is thus set up. The fissile isotope is used up and fission products and plutonium start to accumulate in the uranium. The plutonium itself contributes to fission, though its concentration never approaches that of U^{235} .

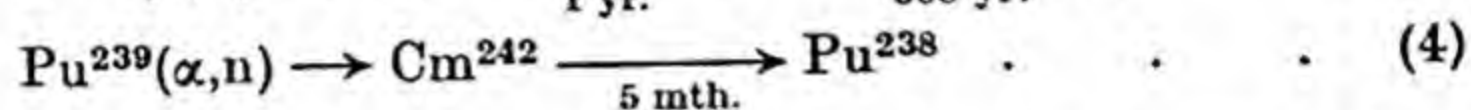
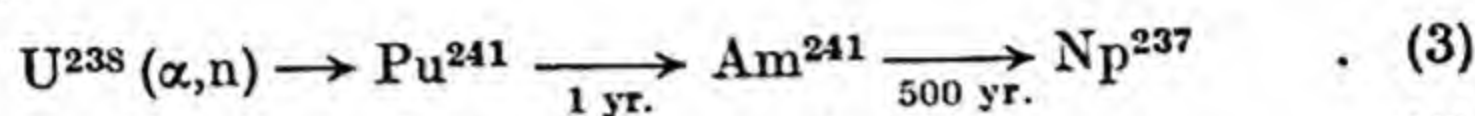
After a time the accumulated fission products, a number of which absorb neutrons readily, upset the delicately balanced neutron economy of the system and the uranium rods are withdrawn and processed chemically in order to separate plutonium. Two other points about the pile are of major importance. Firstly it is necessary to remove from the system the large amount of heat generated in the fission process. This is done either with a gaseous or a liquid coolant. Secondly, the strong neutron flux and the intense radioactivity of the fission products make it necessary to build round the pile a heavy absorbing shield to protect the operators.

The transuranic elements neptunium and plutonium may also be synthesized in cyclotron reactions. Both are formed, for example, following the bombardment of U^{238} with deuterons (1):

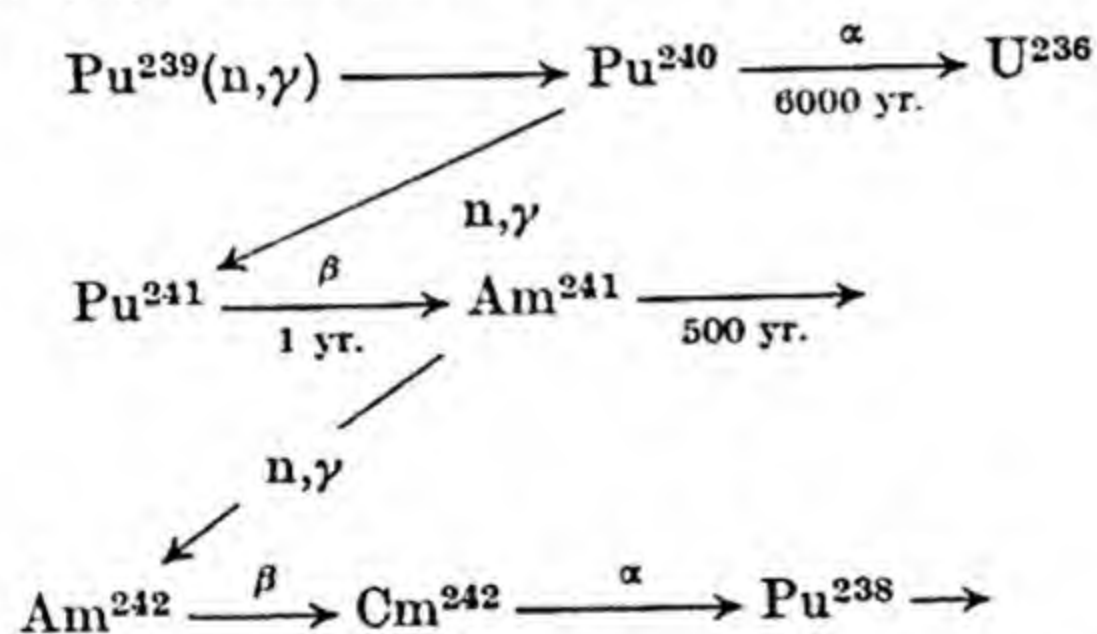


The second reaction, which occurs in the pile, is of special interest because it leads to a neptunium isotope of comparatively long life, which is suitable for chemical studies.

Americium ($Z = 95$) and curium ($Z = 96$) may also be formed in cyclotron reactions, two of which are shown below by way of example (3,4):



Both americium and curium are formed in the pile as secondary products of (n,γ) reactions. This is illustrated below.



The discovery of the transuranic elements berkelium ($Z = 97$) and californium ($Z = 98$) was announced by Seaborg in 1950.¹² When Am^{241} is bombarded with helium ions in the cyclotron it undergoes an $(\alpha, 2n)$ reaction and forms the berkelium isotope Bk^{243} , which decays with a 4.8 hour half-life by electron capture with approximately 1 per cent α -decay branching. The californium isotope Cf^{242} is formed similarly by bombarding the curium isotope Cm^{246} with helium ions. It is an α -active isotope with a half-life of 45 minutes.

The Radioactive Decay Series.—The discovery of the trans-uranic elements has brought about considerable modifications in the classical radioactive decay series. Since α -particle emission leads

¹² Thompson, Street, Ghiorso and Seaborg, *Phys. Rev.*, 1950, **78**, 298; Thompson, Cunningham and Seaborg, *J. Amer. Chem. Soc.*, 1950, **72**, 2798.

Table 2
The $4n$ and $(4n + 1)$ Decay Series

	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96
	Tl	Pb	Bi	Po	At	Rn	Fr	Ra	Ac	Th	Pa	U	Np	Pu	Am	Cm
$4n$ series		212	212	216	220	224	228	232	236							
		208	212			224	228	232	236							
		208	212													
		208	212													
$4n + 1$ series		209	213	217	221	225	229	233	237	241						
		209	213	217	221	225	229	233	237	241						
		209	213	217	221	225	229	233	237	241						
		209	213	217	221	225	229	233	237	241						

to a change of mass of four units it should follow that if all possible masses are to be included, there would be four decay series for masses expressible as $4n$, $4n + 1$, $4n + 2$ and $4n + 3$. Until recently only three were known, namely the thorium ($4n$), uranium ($4n + 2$) and actinium ($4n + 3$) series. The fourth ($4n + 1$) series has now been traced out. It is of special interest because none of its members occur in nature. Isotopes of the transuranics occur in all of these series. They also appear to be more complex, as a result of branching, than was formerly thought to be the case.

The four series in their present form are shown in Tables 2 and 3. The horizontal lines indicate α -particle emissions and the diagonal lines β -particle emissions. Several side branches of the main series involving artificially produced isotopes have been omitted from these tables.

Natural Radioactivity in the Lighter Elements.—Certain of the lighter elements have isotopes which occur naturally and are radioactive. This interesting phenomenon was first observed in the case of potassium, but subsequently several other instances have been found. These are collected together in Table 4.

Table 4
Natural Radioactive Isotopes of the Lighter Elements

<i>Isotope</i>	<i>Disintegration</i>	<i>Half-life</i>	<i>Stable Decay Product</i>
K^{40}	β, K^{12a}	4.5×10^8 yr.	Ca^{40}, A^{40}
Rb^{87}	β	6.0×10^{10} yr.	Si^{87}
Sm^{152}	α	2.5×10^{11} yr.	Nd^{148}
Lu^{176}	β, K	2.4×10^{10} yr.	Hf^{176}, Yb^{176}
Re^{187}	β	4×10^{12} yr.	Os^{187}

Radioactive Elements as Tracers.—The use as tracers of separated or enriched non-radioactive isotopes has been referred to earlier (p. 30) and it was pointed out that only a very limited number of isotopes (those of H, C, N, O, S) are readily available for use in this way. The use of radioactive species has enabled the same principles to be applied on a very much wider scale, since most of the chemical elements have suitable radioactive isotopes. The only limitations to the method are the availability of isotopes, the fact that a few elements (*e.g.* oxygen and fluorine) have no active

^{12a} The letter *K* denotes the capture of a *K* electron by the nucleus. If the resulting nucleus is in an excited state, γ -rays are emitted. The most characteristic radiation accompanying *K* capture is, however, the emission of X-rays when the vacancy in the *K* shell is filled.

isotopes of a conveniently long half-life, and the difficulty of measurement associated with the very soft radiations for some of the isotopes such as C^{14} and S^{35} .

Isotopes of the naturally occurring radioactive elements are of course available for use as tracers and, indeed, were the first to be studied in this way.¹³ Some of the most useful of the artificial radioactive isotopes are given in Table 5. They may in certain cases be obtained as fission products for uranium and in others only by the use of the cyclotron. Quite often alternative modes of preparation are available.

Table 5
Common Radioactive Isotopes used as Tracers

<i>Isotope</i>	<i>Decay</i>	<i>Half-life</i>	<i>Isotope</i>	<i>Decay</i>	<i>Half-life</i>
H^3	β^-	12 yr.	S^{35}	β^-	87.1 day
C^{11}	β^+	20.5 mins.	Ca^{45}	β^-	152 day
C^{14}	β^-	5100 yr.	Fe^{55}	K cap.	4 yr.
Na^{22}	β^+	3.0 yr.	Br^{82}	β^-, γ	34 hr.
Na^{24}	β^-, γ	14.8 hr.	I^{131}	β^-, γ	8.0 day
P^{32}	β^-	14.3 day	Hg^{203}	β^-	43 day

In a limited number of cases radioactive tracers are available in a pure state (carrier-free): more often they are mixed with a certain amount of inactive isotopic material (or carrier), either because separation has not been possible, or to facilitate handling of the minute amounts involved. The methods available for the separation of tracers after their formation vary according to whether

- (a) *The product is isotopic with the target element.* This is so in isotopes produced by (n, γ), (n,2n) or (d,p) reactions. The (n, γ) reactions are of great importance in tracer production since this is the normal reaction taking place in slow neutron irradiation of materials placed in the pile.
- (b) *The product is not isotopic with the target element.* This occurs in the pile with (n,p) and (n, α) reactions and in a number of cyclotron reactions.

In the first of these groups enrichment of the active isotope is possible only in those cases where the Szilard Chalmers effect can be utilized. This depends on the recoil which occurs in a nucleus on the ejection of an α - or β -particle or a photon in a nuclear reaction. When, for example, ethyl iodide is irradiated with neutrons the I^{127} nucleus is transformed to I^{128} by neutron capture. The recoil energy

¹³ Paneth, *Quart. Rev. Chem. Soc.*, 1948, 2, 93; see also Ref. 3.

given to those iodine atoms which react in this way and emit a gamma ray is of the order of 20-100 e.v., which is more than sufficient to break the C—I bond. The active iodine separates and, since it does not recombine or exchange with inactive ethyl iodide, it may be separated by adding a few milligrams of inactive iodine to act as a carrier, reducing and precipitating as silver iodide. The free halogen may also be extracted with a solvent.

The following table gives further examples of the use of the Szilard Chalmers effect :

Table 6

Use of the Szilard Chalmers Effect in Isotope Separation by n,γ Reaction

<i>Substance Irradiated</i>	<i>Product</i>	<i>Remarks</i>
CCl ₄	Cl ³⁸	{ Carrier used, or may be extracted with solvents and other reagents
C ₂ H ₅ Br	Br ⁸²	
Chlorate } Bromate } Iodates }	{ Cl ³⁸ , Br ⁸² I ¹²⁸	{ Product separable as halide ion
Phosphates . . .	P ³²	About half of the activity present as P ^m
Permanganates	Mn ⁵⁶	Most of activity can be removed as MnO ₂
AsH ₃	As ⁷⁶	Activity deposited from gas phase on charged electrodes

When the active isotope sought is not isotopic with the target material the normal range of methods of separation is available. The absolute amount of radioactive material sought is normally small, so that it is advantageous to add some inactive carrier. This, if it is isotopic with the element sought, will facilitate manipulation by increasing the amount of material handled. Quite often, however, non-isotopic carriers are added to carry down small amounts of the radioactive material in precipitation reactions. Inactive copper sulphide, for example, will carry down small quantities of lead, mercury or bismuth.

Ion exchange columns are often used in the isolation of radioactive isotopes, especially in the separation of fission products. Solvent extraction, fractional volatilization, and electrolytic separations all play their part in the solution of the many difficult problems in this field.

Applications of Radioactive Tracers

The possibility of using radioactive elements as indicators for the course of chemical reactions or physical processes arises from the

extreme sensitiveness of the methods of detecting their presence. Using an electroscope as detector, one milligram of thorium may be detected, according to Paneth, by its α -particle activity. Since the rate of emission of α - or β -particles from radioelements varies inversely as the life periods, as little as 10^{-17} grams of the short-lived thorium C could be detected in the same way. By the use of yet more sensitive and quantitative methods of detection—*e.g.* the Geiger counter, which registers the emission of individual α - or β -particles—this infinitesimal figure may even be reduced. It is clear, therefore, that by adding to any normal element a quantity of a radioactive isotope, a very delicate method is opened up for the study of the chemical and physical behaviour of the material.

The interest of the method lies in the means it affords for the study of the normal elements by means of their active isotopes. Using the natural radioelements, thallium may be studied by adding AcC'' ($T_{1/2} = 4.76$ min.), lead by means of additions of RaD ($T_{1/2} = 16$ years) or ThB ($T_{1/2} = 10.6$ hours), and bismuth by means of RaE ($T_{1/2} = 4.85$ days) or ThC ($T_{1/2} = 60.5$ min.). The discovery of artificial radioactivity has greatly extended this field by bringing the lighter elements within its scope.

One example of the application of radioactive indicators is afforded by the discovery of bismuth hydride. By exposing magnesium turnings to thorium emanation, they become impregnated with thorium B and thorium C—isotopes of lead and bismuth, respectively. When such impregnated metal was dissolved in acid, Paneth showed that the radioactivity of the thorium C was transported by the gases evolved, due to the formation of a volatile compound of bismuth—presumably BiH_3 . On passing the gas through a heated tube, the radioactive gas is destroyed, the bismuth isotope being deposited in the heated zone just as is the arsenic or antimony mirror in the Marsh test. Following this demonstration that bismuth hydride could be obtained by dissolving a magnesium-bismuth alloy in acid, Paneth and Winternitz^{13a} succeeded in preparing the hitherto unknown BiH_3 from ordinary bismuth.

In considering the tracer applications of isotopes other than those which occur naturally it must be remembered that the chemistry of the transuranic elements, and of technetium, promethium and astatine, has been largely elucidated by tracer methods. The same is true of polonium and francium. Quite apart from these examples, however, the field is now very large and it is possible to mention only a few examples.

Applications in Analytical Chemistry.—Radioactive tracers are very useful in testing the completeness of analytical separations.

^{13a} *Ber.*, 1918, 51, 1728.

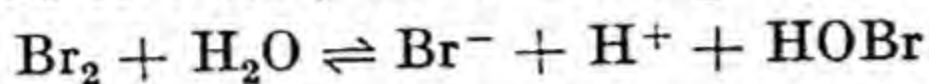
In the precipitation of aluminium with 8-hydroxyquinoline, for example, it is readily established by adding a small amount of radioactive beryllium that the precipitate is contaminated with beryllium if the precipitation is done at a pH 6, but that below this pH there is no contamination. The removal of the last traces of arsenic from germanium in the distillation of GeCl_4 may be followed similarly by the use of a small amount of a radioactive arsenic isotope. Bearing in mind the wide range of active isotopes available, many other such problems, as well as others connected with the washing of precipitates and the solubility of very sparingly soluble substances, will suggest themselves.

It is possible sometimes to detect very small amounts of an impurity in a sample by irradiation of the sample with neutrons or other particles under conditions such that the impurity is converted selectively to a radioactive isotope. The success of the method depends on the impurity having a particularly favourable capture cross-section in the nuclear reaction employed or, if both the impurity and the main component of the mixture are activated, on the possibility of distinguishing the activity due to the impurity. The method has been used *inter alia* for the detection of gallium in iron, copper in nickel, iron in cobalt, and hafnium in zirconium. The activity induced in sodium by neutron irradiation is also easily distinguished and may be used in some cases to detect the presence of the element.

The isotope dilution method may be mentioned as a further illustration of the use of tracers in analytical chemistry. It is useful when a particular component of a complex mixture which has to be estimated can be isolated from the mixture in a pure state, but not quantitatively. The method has been most used in biological studies (*e.g.* in the determination of one particular amino acid in a mixture of several, in which case material enriched in N^{15} would be used). The principle may, however, be illustrated by considering the problem of determining a sodium salt in a complex mixture. To the mixture a quantity of the salt containing a known activity due to Na^{24} is added. The activity of the added material would be known (*e.g.* as the number of counts per mg. under definite counting conditions). After mixing, a small sample of the salt is isolated and its activity remeasured. The count per given weight will now be smaller owing to dilution with the inactive salt in the mixture. The decrease in activity in the recovered sample gives a direct measure of the amount of inactive salt in the mixture, assuming complete isotopic exchange to have occurred.

Reaction Mechanisms.—The study of the mechanism of reactions is probably the most important use of radioactive tracers

in this field. A very simple illustration is the exchange of bromine which occurs when inactive bromine is added to a solution of sodium bromide containing tracer amounts of radioactive bromine ($\text{Br}^{82}; T_{1/2} = 34 \text{ hr.}$). To explain this effect it may be assumed that, on adding bromine to water, the following equilibrium is set up:



Exchange can then occur through the bromide ion. Alternatively it may be supposed that the reaction $\text{Br}^- + \text{Br}_2 \rightleftharpoons \text{Br}_3^-$ provides a medium for the exchange. Many similar studies with radioactive halogens have been made. Thus in carbon tetrachloride there is a rapid exchange of Br_2 and AsBr_3 or SnBr_4 . The bromide ion exchanges rapidly in aqueous solution with $(\text{PtBr}_4)^{-}$ or $(\text{PtBr}_6)^{-}$ and the iodide ion with $(\text{HgI}_4)^{-}$, showing that these complexes must give some free halide ions in solution.

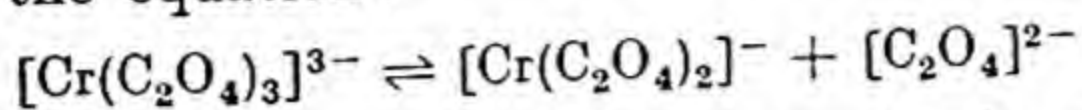
Numerous exchange studies made with oxy-anions have given interesting negative results. For example, there is no exchange of radioactive phosphorus between H_3PO_3 and H_3PO_4 , or arsenic between HAsO_2 and H_3AsO_4 . The ions SO_3^{--} and $\text{S}_2\text{O}_3^{--}$ in solution exchange their sulphur rapidly at 100° , but there is no appreciable exchange at 100° with S^{--} and SO_4^{--} , SO_3^{--} and SO_4^{--} or H_2SO_3 and HSO_4^- . There is a rapid exchange of manganese at room temperature between MnO_4^- and MnO_4^{--} .

Similar in principle is the application of the radioactive isotope of iodine to the problem of the mechanism of the Walden inversion. Optically active *sec*-octyl iodide is racemized with a measurable velocity by sodium iodide in acetone solution. Using radioactive sodium iodide (obtained by irradiation of sodium iodide with neutrons), Hughes, Topley and their associates¹⁴ found that an interchange of radio-iodine between the salt and the *sec*-octyl iodide took place simultaneously. The interchange reaction was checked after a predetermined time by the addition of crushed ice, and the octyl iodide was extracted by means of carbon tetrachloride. Both the organic and the inorganic iodine were then precipitated as silver iodide, and the distribution of the radioactive iodine between the two portions was determined in the usual way, by measuring the intensity of their respective activities. It was thus possible to determine the rate of interchange of iodine between the iodine ions and the alkyl iodide. This reaction velocity agreed, within 10 per cent, with the rate of racemization of the active octyl iodide. It may be concluded, therefore, that the racemization proceeds by way of the same interchange mechanism.

Another interesting example is the mechanism of racemization

¹⁴ *J.C.S.*, 1935, 1525.

of the optically active chromioxalate ion $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$. This occurs in aqueous solution by a fairly rapid first order reaction, and it has been suggested that the rate-determining step is an ionization according to the equation:



An alternative explanation is that an intramolecular rearrangement occurs. When the racemization takes place in a solution which contains oxalate ions with a small proportion of the radioactive isotope C^{11} , no radioactivity finds its way into the chromium complex, which is fairly conclusive evidence against the reaction mechanism involving ionization.

Other Physicochemical Applications.—The use of tracer techniques in ion migration studies is well exemplified by the experiments with astatine (*see* p. 396) in which the element was shown always to form an anion. Tracer methods have also been used in determinations of the diffusion coefficients of more familiar ions (*e.g.* Na^+ and I^-) in solutions.

Diffusion studies in solids have also been made with radioactive tracers, and for measurements of self-diffusion (the migration of the atoms or molecules of a pure solid within the solid) no other method is available. As an example, work on the diffusion of bismuth in bismuth crystals, using the natural bismuth isotope Th-C , may be mentioned. It has been found that the diffusion rate depends on the direction with respect to the crystallographic axes. Similar studies have been made with gold, silver and copper. With gold, for example, it is possible to irradiate one surface of a disc of the metal with resonance neutrons and so obtain on or very near the surface a layer containing radioactive gold atoms. The rate at which this activity penetrates into the metal at various temperatures may then be studied, and the results used to calculate diffusion coefficients.

The specific surface of certain solids may also be studied. If, for example, a given weight of solid lead sulphate is placed in contact with a saturated solution of lead sulphate containing the lead isotope ThB , there will be kinetic exchange of lead between the surface of the solid and the solution, and the activity of the solution will decrease. At equilibrium the following relationship will hold:

$$\frac{\text{ThB on surface}}{\text{ThB in solution}} = \frac{\text{Pb on surface}}{\text{Pb in solution}}$$

The quantities on the left-hand side of the equation may be found from the initial and equilibrium activity of the solution (conveniently measured by the number of counts/c.c.). The lead content

of the solution is also known since the solution is saturated. Thus the absolute weight and the number of atoms of lead at the surface of a given weight of solid is determined. The volume of each molecule of lead sulphate is known, and, assuming the molecule to be a cube, the surface per gram of solid may be derived. This method has been applied with other solids (*e.g.* BaSO_4 , SrSO_4), and in the case of strontium sulphate, similar measurements have also been made with radioactive sulphur in the anion.

Tracers have been used in studying partition coefficients between solvents (*e.g.* for GaCl_3 between aqueous HCl and ether). The vapour pressure of red phosphorus has also been measured by using the 14.3d β -active isotope P^{32} as a tracer.

Applications in Biological Fields.¹⁵—It is not possible to attempt any review of this topic. The fact that radioactive isotopes of carbon, phosphorus and sulphur are readily available is in itself a good indication of the potentialities of the method. Added to these are isotopes of elements such as calcium, iron, iodine and sodium, and also a number of elements which are of importance in traces in certain biological systems. One of the most interesting problems which has arisen has been the synthesis for biological studies of a wide variety of compounds containing radioactive carbon in the molecule. It must also not be forgotten that enriched non-radioactive isotopes of hydrogen, carbon, nitrogen, oxygen and sulphur are available and may be used in much the same way as the radioactive tracers, except, of course, that their assay will (except for deuterium) require the use of a mass spectrograph.

Determination of the Age of Minerals

Four methods have been developed for estimating the age of minerals from their radioactivity. The first of these is based on the measurement of the intensity of coloration in pleochroic haloes which occur in quartz, micas and similar minerals. They are due to the discoloration of the mineral by α -rays from minute particles of radioactive material. The range of the α -rays is only a few thousandths of a centimetre, and the haloes appear under the microscope as a series of concentric rings, each of which represents the action during geological time of α -particles of a particular range. The age determination depends on an estimation of the amount of irradiation necessary to produce a given degree of discoloration, and it is generally agreed that the accuracy is low.

The second method depends on the measurement of the very

¹⁵ See Kamen, *Radioactive Tracers in Biology* (Academic Press Inc., New York, 1947).

small amount of helium present in minerals containing uranium and thorium. This helium is almost certainly formed from α -particles, and in granites and similar rocks of close texture is likely to remain trapped, so that, from its amount, the time during which it has been produced may be calculated. One gram of uranium in equilibrium with its decay products generates roughly 10^{-7} c.c. of helium per year, and the rate of production from thorium is rather less than one-third as great. Thorium is therefore reckoned as equivalent to one-third its weight of uranium. It is necessary to determine the helium in the rock, and also its uranium and thorium contents. If the uranium equivalent per gram of mineral be $(U + 0.3 \text{ Th})$, the age of the mineral in years will be given by the quantity

$$10^7 \times \frac{\text{He (c.c. per gram of mineral)}}{U + 0.3\text{Th}}$$

Some results obtained with rocks of different geological ages are given in Table 7. It is almost certain that some helium will have escaped, so that ages determined by this method represent the lower limit.

Table 7

<i>Geological Age of Rock</i>	<i>Mineral</i>	<i>Source</i>	<i>Age in Million Years</i>
Pliocene	Zircon	Campbell Island, N.Z.	1.5
Miocene	Zircon	Espailly, Auvergne	5.7
Oligocene	Siderite	Niederpleis, Rheinprovinz	7.0
Upper Carboniferous .	Limonite	Forest of Dean	128
Devonian	Haematite	Caen	112
Silurian	Thorianite	Ceylon	226
Middle Pre-Cambrian	Sphene	Arendal, Norway	329
Lower Pre-Cambrian	Zircon	Renfrew Co., Ontario	543

A third method depends on the determination of the ratio of uranium to Pb^{206} in the mineral. This lead isotope is the end product of the uranium decay series, and its amount will be proportional to the age of the mineral. The rate of formation follows from the decay constant of uranium. The isotopic composition of the lead should be checked with the mass spectrograph and, if necessary, the amount of lead determined analytically corrected for other lead isotopes present. It is also necessary in the case of older minerals to allow for the decay of the uranium. Ages determined

by this method range up to $1 - 3 \times 10^9$ years. The determination may likewise be based on the ratio of thorium to Pb^{208} .

The age of a mineral may also be estimated by determining the ratio $\text{Pb}^{206} : \text{Pb}^{207}$. This ratio is used because U^{238} and U^{235} , the parents of the decay series which lead to Pb^{206} and Pb^{207} , have half-lives which are markedly different (4.51×10^9 yr. and 7.07×10^8 yr. respectively). This implies that in the older minerals there will be a lower ratio of Pb^{206} to Pb^{207} .

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